

**LIGATIONAL BEHAVIOR OF THIOMOLYBDATES
AND THIOTUNGSTATES TOWARDS Mn(II), Fe(II),
Co(II), AND Ni(II) IN THE PRESENCE OF
AROMATIC DIIMINES**

**A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY**

**by
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**to the
DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR**

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STATEMENT

I hereby declare that the matter embodied in this thesis "Ligational Behavior of Thiomolybdates and Thiotungstates Towards Mn(II), Fe(II), Co(II) and Ni(II) in the Presence of Aromatic Diimines", is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Dr. S. Sarkar.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.


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CERTIFICATE

Certified that the work "Ligational Behavior of Thio-molybdates and Thiotungstates Towards Mn(II), Fe(II), Co(II) and Ni(II) in the Presence of Aromatic Diimines", presented in this thesis has been carried out by Mr. B. R. Srinivasan under my supervision and the same has not been submitted elsewhere for a degree.



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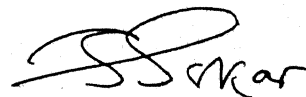
This is to certify that Mr. B. R. Srinivasan has satisfactorily completed all the courses required for the Ph.D. degree program. The courses include:

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LIST OF ABBREVIATIONS

Å	Angstrom unit, 10^{-10}m
bipy	2,2'-bipyridine
br	bridging
cm^{-1}	Wavenumber
conc.	Concentrated
DMF	N,N'-Dimethylformamide
EPR	electron paramagnetic resonance
EXAFS	Extended X-ray Absorption Fine Structure
IR	Infrared
M	Mo, W
M'	Metal coordinated to $(\text{MS}_4)^{2-}$
MO	Molecular Orbital
nm	nanometer 10^{-9}m
NMF	N-Methylformamide
o-phen	1,10-Phenanthroline
Ph	phenyl
ν	Frequency, stretching vibration (subscripts s and as denote symmetric and asymmetric)
term	Terminal

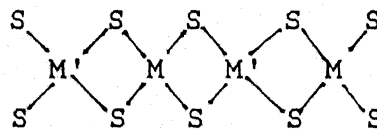
SYNOPSIS

The thesis entitled, "Ligational Behavior of Thiomolybdates and Thiotungstates Towards Mn(II), Fe(II), Co(II) and Ni(II) in the Presence of Aromatic Diimines", consists of five chapters.

The first chapter presents an overview of the literature on thiomolybdates and thiotungstates. A systematic survey of these compounds encompassing their synthetic aspects, physical properties, chemical reactivity and spectroscopic investigations has been described. The importance of Fe-M-S complexes as models for the molybdenum site of the enzyme nitrogenase and M'-M-S complexes in hydrodesulfurization catalysts (M = Mo, W; M' = Co, Ni) has been mentioned.

The second chapter outlines the scope of the present work. The thiomolybdates and thiotungstates are purely inorganic chelate ligands and give rise to novel multimetallic complexes. The aqueous reactions of the thiometallates with bivalent metal salts are known to produce bis(thiometallato) complexes of the type $[M'(MS_4)_2]^{2-}$ (M' = Fe, Co, Ni, Pd, Pt, Zn, Cd, Hg; M = Mo, W) which can be trapped by bulky organic cations. However, in the absence of

bulky cations, catena units of the type



and amorphous metal sulfides of the type MS_3 and $M'S$ are formed. A synthetic strategy to prevent this polymerization and sulfide formation, and to produce discrete heterometal complexes has been

outlined. The strategy involves the use of aromatic diimine complexes of the bivalent metals instead of the simple metal salts. This method has been successfully applied to Mn(II) for the first time, resulting in the formation of a Mn-Mo/W complex stitched by sulfur bridges.

The third chapter presents the experiments directed towards this research endeavour and has been divided into eight sections. Section 3.1 describes the methods of analysis and the work-up manipulations of the newly prepared complexes. Section 3.2 presents the procedures for the preparation of the free thiometallates. Sections 3.3, 3.4, 3.5 and 3.6 describe the syntheses of the hexacoordinate thiometallato complexes of Mn(II), Fe(II), Co(II) and Ni(II) respectively. All the hexacoordinate complexes reported in this work have the general formula $[L_2M'(\mu-S)_2MS_2]$ ($M = Mo, W$; $M' = Mn, Fe, Co, Ni$; $L = 2,2'$ -bipyridine, 1,10-phenanthroline). Section 3.7 details the procedures for the synthesis of the tetracoordinate Ni(II) thiometallato complexes. All the bimetallic complexes reported in this work are 1:1 complexes. Section 3.8 deals with the synthetic aspects and reactivity of the newly prepared complexes. The reaction of $(L_3M')^{2+}$ ($M' = Mn, Fe, Co, Ni$; $L =$ aromatic diimine) with $(MS_4)^{2-}$ ($M = Mo, W$) to yield the neutral, bimetallic, mixed ligand complex $[L_2M'(\mu-S)_2MS_2]$ can be termed as a simple ligand-displacement reaction. However, when $M' = Fe$ and $L = 1,10$ -phenanthroline, the ligand displacement reactions do not occur.

The physico-chemical and structural investigations of the newly prepared complexes have been discussed in chapter 4. The complexes have been studied by vibrational, electronic and electron paramagnetic resonance spectroscopy, cyclic voltammetry, magnetic susceptibility measurements and X-ray powder diffraction. The bidentate nature of the thiometallate ligands in these complexes, has been convincingly proved by means of infrared spectral analysis. The tetracoordinate mixed-ligand nickel(II) complexes are diamagnetic and hence inferred to have square-planar arrangement. All the hexacoordinate complexes reported in this thesis are isotypic. An attempt has been made to understand the relative ligand field strength of the anionic ligands $(MS_4)^{2-}$ and $(MOS_3)^{2-}$ ($M = Mo, W$) in these systems.

The final chapter summarises the results of the present work. A few of the important results are as follows.

- i) The reaction of aromatic diimine complexes of bivalent metals with thiometallates results in the formation of discrete heterometal complexes. The generality of such a reaction has been tested with some first row bivalent transition metal ions.
 - ii) The first example of a Mn-M ($M = Mo, W$) complex stitched via sulfur bridges, is reported.
 - iii) $(MOS_3)^{2-}$ is a stronger ligand compared to $(MS_4)^{2-}$ ($M = Mo, W$).
- The thesis ends with some recommendations for future work.

CHAPTER 1

INTRODUCTION

Interest in sulfur containing compounds of molybdenum and tungsten has grown with respect to their implications in bioinorganic chemistry and catalysis [1,2]. Molybdenum has a high affinity for sulfur as can be seen from the natural occurrence of molybdenum as molybdenite and a variety of sulfur rich molybdenum compounds prepared till date.

Sulfur can replace oxygen isomorphously in several compounds but such substitutions when applied to molybdenum often leads to the formation of molybdenum-sulfur compounds entirely unrelated to those containing only oxygen [3]. Many oxygen containing molybdenum compounds have no corresponding sulfur analogs as in the case of the heteropoly and isopoly compounds [4]. Similarly the oxo-peroxo analogs of poly(thiomolybdates) like $[\text{Mo}_3\text{S}_{13}]^{2-}$, $[\text{Mo}_2\text{S}_{12}]^{2-}$, and $[\text{Mo}_2\text{S}_{11}]^{2-}$ are unknown.

In the case of simple molybdates $[\text{MoO}_4]^{2-}$ and tungstates $[\text{WO}_4]^{2-}$ partial or total substitution of oxygen by sulfur has been effected. The thiomolybdates and thiotungstates derived by the sulfur substitution from the oxo analogs have interesting chemical properties and occupy a special position in coordination chemistry as they are unique ligands which are purely inorganic in nature and give rise to sulfur bridged multimetallic complexes.

A brief review of molybdenum sulfur chemistry with special reference to thiomolybdates is presented below. The chemistry of the corresponding tungsten compounds which differs considerably, has also been incorporated, for comparison.

The existence of many molybdenum sulfides has been reported in the literature. Of these only the disulfides MS_2 , the trisulfides MS_3 , $[M = Mo, W]$ and the sesquisulfide Mo_2S_3 are well established. These compounds have useful solid state properties and their chemistry has been extensively reviewed [5]. The solution chemistry of these sulfides is unknown owing to their high insolubility and mainly solid state studies have been carried out.

The amorphous trichalcogenides MX_3 ($M = Mo, W$; $X = S, Se$) have interesting electrochemical and physical properties. The structures of these trichalcogenides have been investigated by X-ray absorption spectroscopy. The EXAFS studies clearly demonstrate metal-metal bonding in all the MX_3 compounds examined [6]. The structural changes that take place during the lithiation of the X-ray amorphous materials, MX_3 have been recently studied by EXAFS analysis [7] and an increase in the number of metal-metal bonds and a significant decrease in the metal-metal distance have been observed. Based on these observations, a reasonable structure for the fully lithiated Li_4MoS_3 has been proposed.

1.1 Thiomolybdates and thiotungstates:

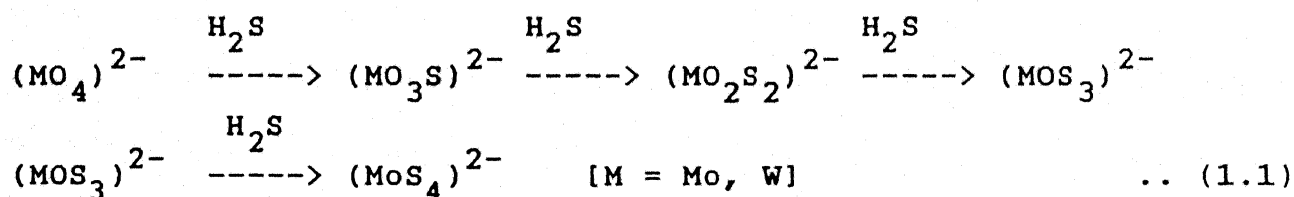
The thiomolybdates and thiotungstates constitute an important area of inorganic molybdenum/tungsten-sulfur chemistry, owing to their versatile reactivity. The subject matter of the

thesis being the ligational behavior of thiomolybdates and thio-tungstates, a systematic chemistry of these compounds encompassing their synthetic aspects, physical properties, chemical reactivity, spectroscopic investigations, uses and relevance in bioinorganic chemistry known till date is briefly outlined.

The first report on thiomolybdates appeared in the literature as early as 1826, when Berzelius investigated their formation by passing hydrogen sulfide gas into aqueous solutions of molybdate $[\text{MoO}_4]^{2-}$ or tungstate $[\text{WO}_4]^{2-}$ [8]. Sixty years later Kruss [9] and Corleis [10] reported the synthesis of $(\text{NH}_4)_2\text{MoS}_4$ and $(\text{NH}_4)_2\text{WS}_4$ respectively. However, most of the work in this area has been done only in the later half of this century primarily by Müller and coworkers [11,12].

1.2 Synthesis of thiomolybdates and thiotungstates:

Thiomolybdate and thiotungstate anions are prepared by the reactions of oxomolybdate or oxotungstate anions with hydrogen sulfide in basic aqueous solutions [13,14]. The reaction can be represented as follows:



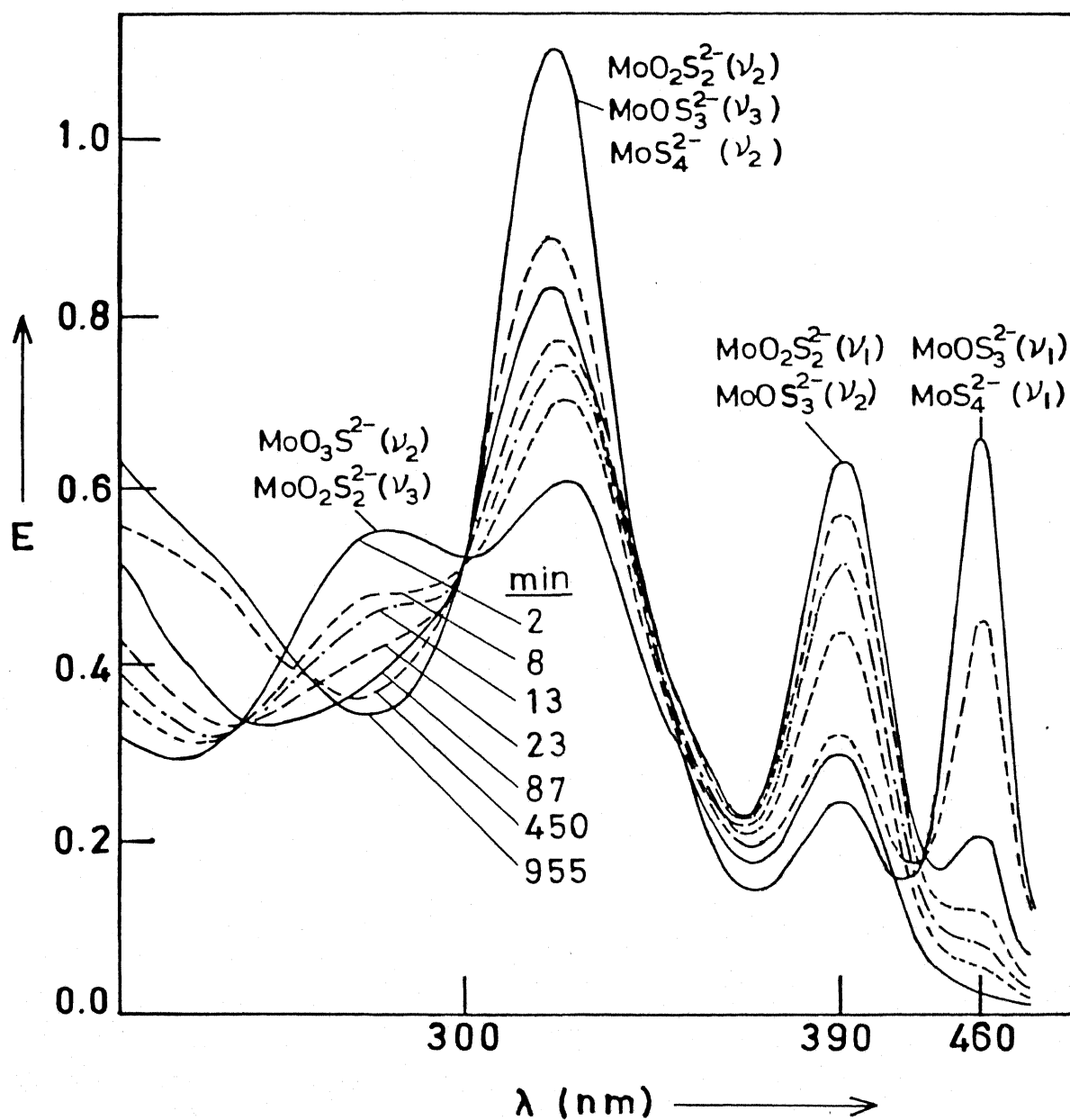
All the thiometallates (the term thiometallate refers to any of the thioanions of the formula $[\text{MO}_{4-n}\text{S}_n]^{2-}$ ($\text{M}=\text{Mo}, \text{W}; n=1-4$) throughout this thesis) have strong and characteristic absorption bands in the uv-vis region and hence the reactions in which they are formed and decomposed can be followed by spectrophotometric methods. The kinetics of thiometallate formation has been inves-

tigated by many authors [15-17]. The electronic spectra of the $(\text{MoO}_4)^{2-}/\text{H}_2\text{S}$ reaction system as a function of time is presented in Fig. 1.1 [16].

When hydrogen sulfide gas is passed into an aqueous solution of oxometallate a change in the electronic spectrum is observed. The bands characteristic of all the species $[\text{MO}_{4-n}\text{S}_n]^{2-}$ ($n=1-4$) appear in succession. From the existence of isobestic points it follows that almost only two species can coexist in the solution at any one time. In order to isolate any one of the species a cation that forms a sparingly soluble salt with any one of the species should be added. Based on this principle, the oxotrithiomolybdate has been salted out as the cesium salt.

The duration of hydrogen sulfide gas passing, the temperature, the concentration, and the counter cation used are all important factors to be considered for the preparation and isolation of the various thiometallates. The monothioanions have been shown to exist only in solution and pure compounds have not been isolated [18,19]. The dithiometallates are prepared from cold oxometallate solutions. The trithiometallates can be easily prepared as the cesium salts. The $[\text{MoO}_4]^{2-}$ ion forms the tetrathio species readily, while the preparation of tetrathiotungstate requires drastic reaction conditions (60°C , 9 h) [14].

The alkali metal and ammonium salts of the thiometallates range from yellow to red in color and are soluble in water, the solubility decreasing in going from Na^+ to Cs^+ salts. The quaternary ammonium, phosphonium, arsonium XR_4^+ ($\text{X} = \text{N}, \text{P}, \text{As}$; $\text{R} = \text{aryl or alkyl}$) salts of the thiometallates are soluble in organic

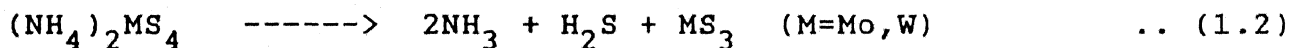


THE ELECTRONIC SPECTRA OF THE $\text{MoO}_4^{2-}/\text{H}_2\text{S}$ SYSTEM AS A FUNCTION OF TIME.

FIG. 1-1

solvents. The stability of the thiometallates decreases with increasing oxygen content. Thus the dithiometallates are readily hydrolyzed by water. Further, the thiometallates are not very stable in aqueous solution especially at low pH. They decompose slowly in mineral acids to form the 'X-ray amorphous' sulfides. The physical properties of some salts of thiometallates are listed in Table 1.1.

Most of the alkali metal and ammonium thiometallates crystallize in the β -K₂SO₄ type structure. The [MS₄]²⁻ ion is tetrahedral like the [SO₄]²⁻ ion [20-22]. On heating, the ammonium tetrathiometallates decompose to give ammonia, hydrogen sulfide and the amorphous trisulfide as given in eq. (1.2) [23,24].



1.3 Reactivity of thiomolybdates and thiotungstates:

The thiometallates are versatile reagents in inorganic synthesis and undergo a variety of reactions with various reagents. These reactions can be broadly classified into two types.

- i. Reactions of thiometallates resulting in the formation of sulfur rich poly(thiometallates).
- ii. Reactions of thiometallates resulting in the formation of heterometal aggregates.

1.4 Formation of poly(thiometallates):

The sulfur rich poly(thiometallates) are formed from the reactions of the thiometallates with, a) polysulfide b) elemental sulfur c) thiols d) organic disulfides and e) acid. A number of poly(thiometallates) have been synthesized and structurally

Table 1.1

Physical properties of some thiometallates

Salt	Color	Stability
$(\text{NH}_4)_2\text{MoO}_2\text{S}_2$	Orange	Stable in air
$(\text{NH}_4)_2\text{WO}_2\text{S}_2$	Yellow	Stable in air
$\text{Ni}(\text{NH}_3)_6\text{MoO}_2\text{S}_2$	Yellow	Decomposes slowly
$\text{Ni}(\text{NH}_3)_6\text{WO}_2\text{S}_2$	Light yellow	Decomposes slowly
$\text{I}_2\text{MoO}_2\text{S}_2$	Orange	Stable in air
$\text{I}_2\text{WO}_2\text{S}_2$	Yellow	Stable in air
S_2MoOS_3	Red-orange	Stable in air
S_2WOS_3	Yellow	Stable in air
I_2MoOS_3	Red-orange	Stable in air
I_2WOS_3	Deep yellow	Stable in air
$\text{Ni}(\text{NH}_3)_6\text{MoOS}_3$	Orange-yellow	Stable in dry air
$\text{Ni}(\text{NH}_3)_6\text{WOS}_3$	Green-yellow	Stable in dry air
$(\text{NH}_4)_2\text{MoS}_4$	Red	Stable in dry air
$(\text{NH}_4)_2\text{WS}_4$	Orange-yellow	Stable in dry air
S_2MoS_4	Red	Stable in dry air
S_2WS_4	Yellow	Stable in dry air
$\text{Ph}_4\text{P})_2\text{MoS}_4$	Red	Stable in dry air
$\text{Ph}_4\text{P})_2\text{WS}_4$	Yellow	Stable in dry air
$\text{Ni}(\text{NH}_3)_6\text{MoS}_4$	Orange-red	Moderately stable in dry air
$\text{Ni}(\text{NH}_3)_6\text{WS}_4$	Lemon-yellow	Stable in dry air
$\text{Co}(\text{NH}_3)_6\text{MoS}_4$	Yellow-red	Decomposes slowly
$\text{Co}(\text{NH}_3)_6\text{WS}_4$	Green-yellow	Decomposes slowly

characterized in recent years. The facile formation of these sulfur rich species is a clear indication of the high affinity of molybdenum or tungsten in different oxidation states for sulfur.

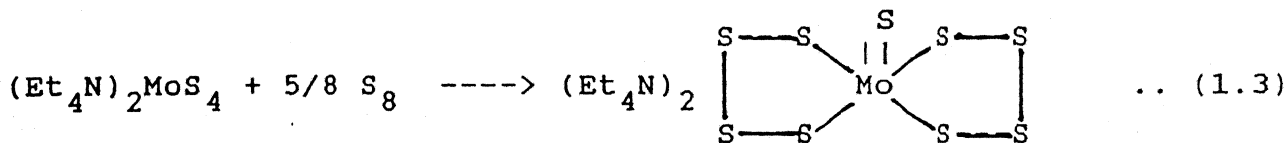
1.4.1 Reactions of thiometallates with polysulfide:

The first sulfur rich molybdenum compound $[\text{Mo}_2\text{S}_{12}]^{2-}$, the only known compound with exclusively $(\text{S}_2)^{2-}$ ligands has been prepared by reducing molybdate with polysulfide solution containing a high proportion of $(\text{S}_2)^{2-}$ ion [25]. However, the same reaction when carried out at higher temperatures [26-28] yields the trimeric cluster $[\text{Mo}_3\text{S}_{13}]^{-2}$. The formation of the above mentioned sulfur rich species involves both condensation and reduction of molybdenum. Eventhough the preparation of these sulfur rich species is achieved starting from oxomolybdate, tetrathiomolybdate is formed in situ which undergoes further reaction to give the final products. The synthesis of $[\text{Mo}_2\text{S}_{12}]^{2-}$ and $[\text{Mo}_3\text{S}_{13}]^{2-}$ has also been effected by starting from tetrathiomolybdate instead of oxomolybdate. In contrast to this, $[\text{WS}_4]^{2-}$ does not react with polysulfide.

The reaction of oxomolybdate with aqueous ammonium polysulfide solution in the presence of hydroxylamine leads to the formation of several interesting polynuclear nitrosyl-molybdenum-sulfido clusters. Müller and coworkers have used this strategy and reported the preparation of some unusual compounds like $[\text{Mo}_4(\text{NO})_4\text{S}_{13}]^{4-}$, $[\text{Mo}_4(\text{NO})_4\text{S}_{12}\text{O}]^{2-}$ and $[\text{Mo}_2(\text{NO})_2(\text{S}_2)_3\text{S}_5(\text{OH})]^{3-}$ from various combinations of hydroxylamine, molybdate and polysulfide [29-32].

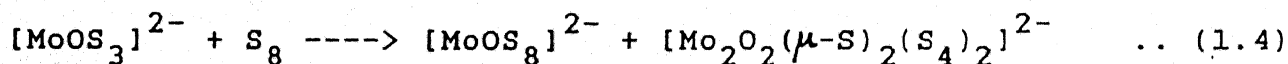
1.4.2 Reactions of thiometallates with elemental sulfur:

Elemental sulfur reacts readily with $[\text{MoS}_4]^{2-}$ under ambient conditions to form the novel sulfur ring complex $[\text{MoS}_9]^{2-}$ in excellent yields, as in eq. (1.3) [33-35].



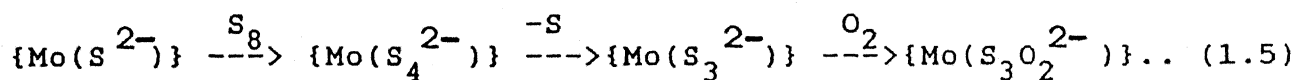
The above reaction can also be carried out using dibenzyltrisulfide as the source of sulfur. The oxidation of the coordinated S^{2-} to $(\text{S}_4)^{2-}$ and the coupled reduction of Mo(VI) to Mo(IV) are brought about by elemental sulfur by an induced electron transfer pathway, wherein the electron transfer occurs from the coordinated S^{2-} to the molybdenum center.

The attempts to exchange the $(\text{Et}_4\text{N})^+$ cations in $(\text{Et}_4\text{N})_2\text{MoS}_9$ with $(\text{PPh}_4)^+$ has resulted in the formation of an altogether different compound $(\text{PPh}_4)_2[\text{Mo}_2\text{S}_{10}]$ [34]. This dianion $[\text{Mo}_2\text{S}_{10}]^{2-}$ has also been obtained by the sulfur abstraction from $[\text{Mo}_2\text{S}_{12}]^{2-}$ with PhSNa [36]. The hydrolysis of $[\text{MoS}_9]^{2-}$ yields the oxo-product, $[\text{MoOS}_8]^{2-}$. The reaction of sulfur with $[\text{MoOS}_3]^{2-}$ also yields the oxo compound, $[\text{MoOS}_8]^{2-}$, alongwith the dimeric complex $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_4)_2]^{2-}$ as a minor product.



From a DMF solution containing $(\text{PPh}_4)_2\text{MoOS}_3$ and elemental sulfur after exposure to air, the novel compound containing the dithiosulfate ligand, $[(\text{S}_2)\text{OMoS}_2\text{Mo}(\text{O})(\text{S}_3\text{O}_2)]^{2-}$, has been isolated [37]. The formation of the dithiosulfate ligand may

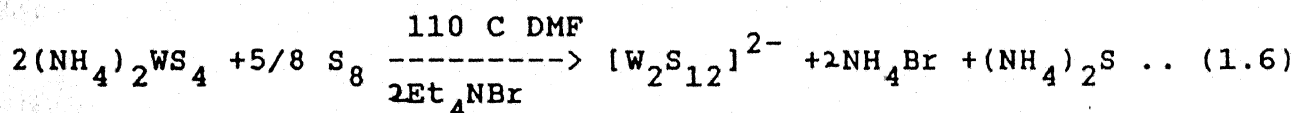
probably proceed according to eq(15) in which the oxidation of the coordinated $(S_3)^{2-}$ ligand is involved.



$[MoS_9]^{2-}$ reacts with CS_2 to give perthiocarbonato complexes $[MoS_9]^{2-}$ appears to function as a source of $[MoS(S_2)_2]^{2-}$ in these reactions and two isomers of $[MoS(CS_4)_2]^{2-}$ are obtained [38]. The reaction of $[MoS_9]^{2-}$ with activated acetylenes like dimethoxyacetylene dicarboxylate (DMAD) results in the formation of the trigonal prismatic tris(dithiolene) complex [39,40].

Even though $[WS_9]^{2-}$ has not been isolated from the reaction of $[WS_4]^{2-}$ with elemental sulfur in contrast to the molybdenum case, the in situ formation of this elusive species is indicated by the formation of $[W(\text{dithiolene})_3]^{2-}$ complex in the reaction of $[WS_4]^{2-}$ with elemental sulfur in the presence of activated acetylenes as has been observed with the Mo analogs [41].

The reaction of ammonium tetrathiotungstate with elemental sulfur at elevated temperatures ($110^\circ C$) in DMF leads to the formation of the dimeric W(V) complex as shown below [42].



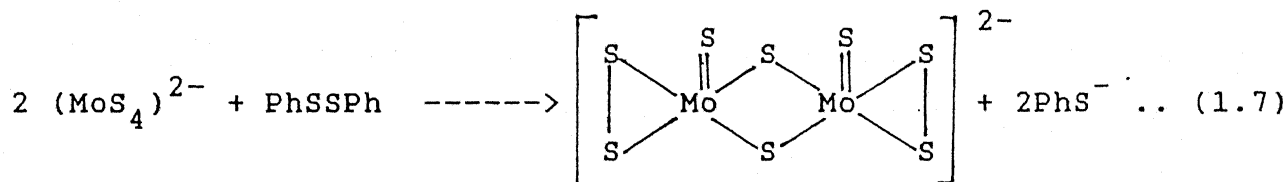
An important point to be noted in the above reaction is the purging of argon or nitrogen above the solution during the reaction. Failure to purge the system results in significantly reduced yields of the dimer and reisolation of the starting material. This is not surprising because $(NH_4)_2S$, one of the

products of the reaction, can combine with sulfur to form polysulfide which can oxidize the W(V). The above point gains credence from the fact that $[\text{WS}_4]^{2-}$ does not show any reactivity with polysulfide unlike $[\text{MoS}_4]^{2-}$.

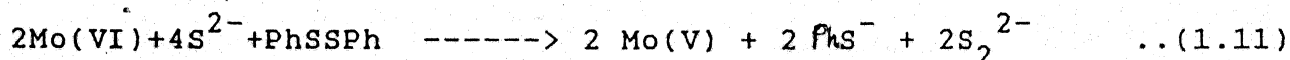
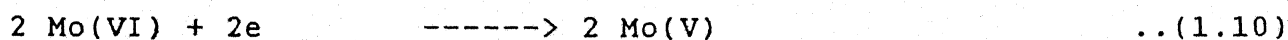
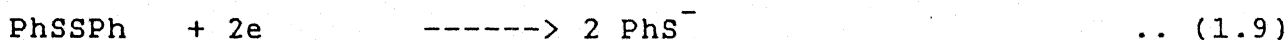
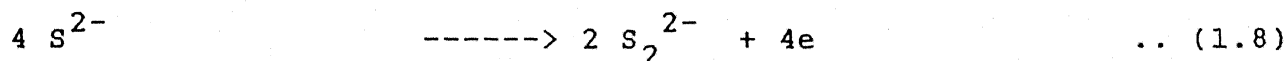
The molybdenum analog of $[\text{W}_2\text{S}_{12}]^{2-}$ has been prepared by essentially following the same procedure as for the W analog but at a lower temperature (95 °C) [42]. The structure of the dimeric species $[\text{M}_2\text{S}_{12}]^{2-}$ (M=Mo,W) consists of a syn- $\text{M}_2\text{S}_2(\text{M}-\text{S})_2^{2+}$ core coordinated by two bidentate tetrasulfido $(\text{S}_4)^{2-}$ ligands.

1.4.3 Reactions of Thiometallates with Organic Disulfides:

The reaction of ammonium tetrathiomolybdate with PhSSPh in DMF at 90 °C results in the dimerisation of $(\text{MoS}_4)^{2-}$ to give $[\text{Mo}_2\text{S}_8]^{2-}$ as given in eq.(1.7) [43,44].

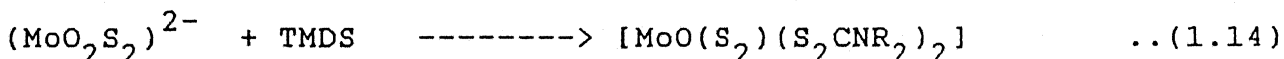
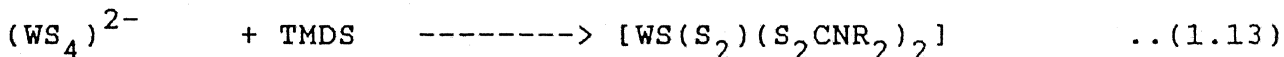
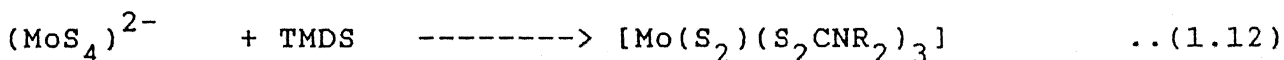


The above reaction where the metal center has been reduced by one electron and the organic disulfide by two electrons can be termed as an example of an induced electron transfer reaction. For "bookkeeping purposes" the following redox reactions can be envisaged.



The four electrons required for the formation of each $[\text{Mo}_2\text{S}_8]^{2-}$ are provided by the oxidative coupling of four sulfide anions to two disulfide ligands. The conversion of $[\text{MoS}_4]^{2-}$ to $[\text{Mo}_2\text{S}_8]^{2-}$ can also be effected by diphenyldiselenide at 90°C or $[\text{p-NO}_2\text{C}_6\text{H}_4\text{SSC}_6\text{H}_4\text{NO}_2\text{-p}]$ at room temperature. The tungsten analog $[\text{W}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ has also been prepared by the oxidation of $(\text{NH}_4)_2\text{WOS}_3$ with elemental iodine [45].

The reaction of thiometallates with tetraalkylthiuram disulfides (TMDS) yields dithiocarbamate complexes. An eight coordinate Mo(V) complex is obtained by the reaction of $[\text{MoS}_4]^{2-}$ with TMDS as in eq (1.12). On the contrary, the reactions of $[\text{WS}_4]^{2-}$ and $[\text{MoO}_2\text{S}_2]^{2-}$ with TMDS result in the formation of a seven coordinate W(VI) and Mo(VI) complexes respectively [44,46].



The above reactions clearly indicate that the formation of the Mo(V) dithiocarbamate complex involves an internal metal-ligand redox process, while the formation of the W(VI) complex involves purely a ligand based redox reaction.

1.4.5 Reactions of thiometallates with thiols:

The reaction of ammonium tetrathiomolybdate in DMF with thiophenol under argon at 90°C , yields the black trinuclear species $[\text{Mo}_3\text{S}_9]^{2-}$ in good yields [47]. The W analog $[\text{W}_3\text{S}_9]^{2-}$ has also been obtained by an analogous procedure at higher temperatures ($110\text{--}130^\circ\text{C}$). With mercaptans like, 1,2-ethanedithiol

(edth₂) and o-aminobenzenethiol(abth₂), thiolato complexes of the type $[M_2S_4(edt)_2]^{2-}$ and $[M_2S_4(abt)_2]^{2-}$ [47,48] are formed. These reactions do not take place when $(XR_4)_2MoS_4$ (X=N,P,As) is used as the starting material, indicating the need for a proton source.

1.4.5 Reaction of thiometallates with acids:

The condensation reactions of oxometallates in aqueous solutions have been well studied in contrast to the very little work done on thiometallates. The condensation reactions subsequent to the protonation of thiometallate ions take place at a lower pH than that of the oxoanions, since the proton affinity of sulfur is appreciably lower than that of oxygen. Further, the investigations with thiometallates are more difficult owing to the formation of the amorphous trisulfides at low pH [12].

The dimeric dianion $[Mo_2OS_7]^{2-}$ is the only product to have been isolated as the tetra n-butylammonium salt, by the reaction of $[MoS_4]^{2-}$ with hydrochloric acid in air [48]. The dimeric dianion $[Mo_2OS_7]^{2-}$ has also been recently synthesized by Sarkar and coworkers just by heating $(NH_4)_2MoS_4$ in air which involves induced electron transfer [50]. Yet another report [51] describes the preparation of the same compound $[Mo_2OS_7]^{2-}$, from an ill-defined mixture consisting of cobalt sulfate, $[CoS_4]^{2-}$ and $NaBH_4$. Interestingly cobalt has not been incorporated into the system even though cobalt-thiometallate complexes are known.

The dinuclear molybdenum species $[Mo_2O_2S_6]^{2-}$ is formed by the aging of $(NH_4)_2MoS_4$ [50]. The aging process is hastened in the laboratory atmosphere and hence only freshly prepared samples of $(NH_4)_2MoS_4$ should be used while studying its reactions.

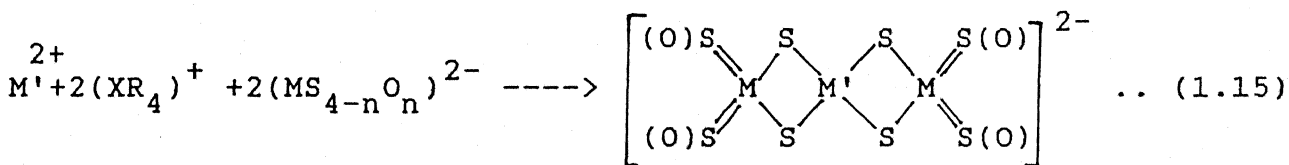
The condensation behavior of $[\text{WS}_4]^{2-}$ differs considerably from that of $[\text{MoS}_4]^{2-}$, since protonation takes place at relatively low pH values. When an aqueous solution of tetrathiotungstate is acidified a mixture of condensed species like $[\text{W}_3\text{OS}_8]^{2-}$, $[\text{W}_3\text{S}_8]^{2-}$, $[\text{W}_4\text{S}_{12}]^{2-}$ are formed besides $[(\text{HS})\text{WS}_3]^-$ [52,53]. The isolation of a particular poly(thiotungstate) depends on the reaction conditions employed and the counter cations used. S  cheresse and coworkers have reported the synthesis of poly(thiotungstate) species like $[\text{W}_4\text{S}_{12}]^{2-}$, $[\text{W}_2\text{S}_{11}\text{H}]^-$ by reaction of $(\text{PPh}_4)_2\text{WS}_4$ dissolved in either acetonitrile or dichloromethane with hydrochloric acid or acetic acid [54,55]. The reduction of an acidified solution of tetrathiotungstate with NaBH_4 results in the formation of the incomplete cubane type $[\text{W}_3\text{S}_4]^{4+}$ aqua ion [56].

An attempted synthesis of $[\text{Mn}(\text{WS}_4)_2]^{2-}$ from $(\text{PPh}_4)_2\text{WS}_4$ in acetonitrile acidified with small amounts of glacial acetic acid in the presence of manganous chloride has resulted in the formation of a pure binary W-S species $[\text{W}_2(\mu\text{-S})(\text{S})_2(\text{S}_2)_4]^{2-}$ [57]. When LiCl was used $[\text{W}_3\text{S}_9]^{2-}$ was isolated and the use of CrCl_3 resulted in the formation of $[\text{W}_4\text{S}_{12}]^{2-}$. When $(\text{PPh}_4)_2\text{MoS}_4$ was used in the above reaction with MnCl_2 only the complex $[\text{Mo}_3\text{S}_9]^{2-}$ was isolated. In all the above cases the hetero metal has not been incorporated into the Mo/W-S system. The role of manganese to bring about the formation of $[\text{W}_2\text{S}_{11}]^{2-}$ is not clearly known. The synthesis of the closely related molybdenum analog $[\text{Mo}_2\text{O}_2(\mu\text{-S})(\text{S}_2)_4]^{2-}$ has been recently reported by the oxidation of $[\text{MoOS}_8]^{2-}$ with $[\text{Cp}_2\text{Fe}]^+$ [58].

1.5 Heterometal aggregates:

The utility of tetrathiomallates as purely inorganic chelating ligands started with the reported synthesis of the bis-(tetrathiotungstato)nickelate(II) anion $[\text{Ni}(\text{WS}_4)_2]^{2-}$ [58]. Müller and coworkers have studied the ligational behavior of the thiomallates and synthesized several heteronuclear complexes where the central metal ion can be either a transition metal or a non-transition metal and the thiomallate can be any member of the series $(\text{MS}_{4-n}\text{O}_n)^{2-}$ [$\text{M}=\text{Mo}, \text{W}$; $n=0-2$] [11,12,59-66].

The preparation of the bis(thiomallato) complexes involves the reaction of bivalent metal salts in the presence of a bulky cation with thiomallates in aqueous medium. The general reaction for the formation of bis(thiomallato)metal complexes can be written as follows:



where $\text{M}'=\text{Fe}, \text{Co}, \text{Ni}, \text{Pd}, \text{Pt}, \text{Zn}, \text{Cd}, \text{Hg}$; $\text{M}=\text{Mo}, \text{W}$; $\text{X}=\text{As}, \text{P}$; $n=0, 1, 2$

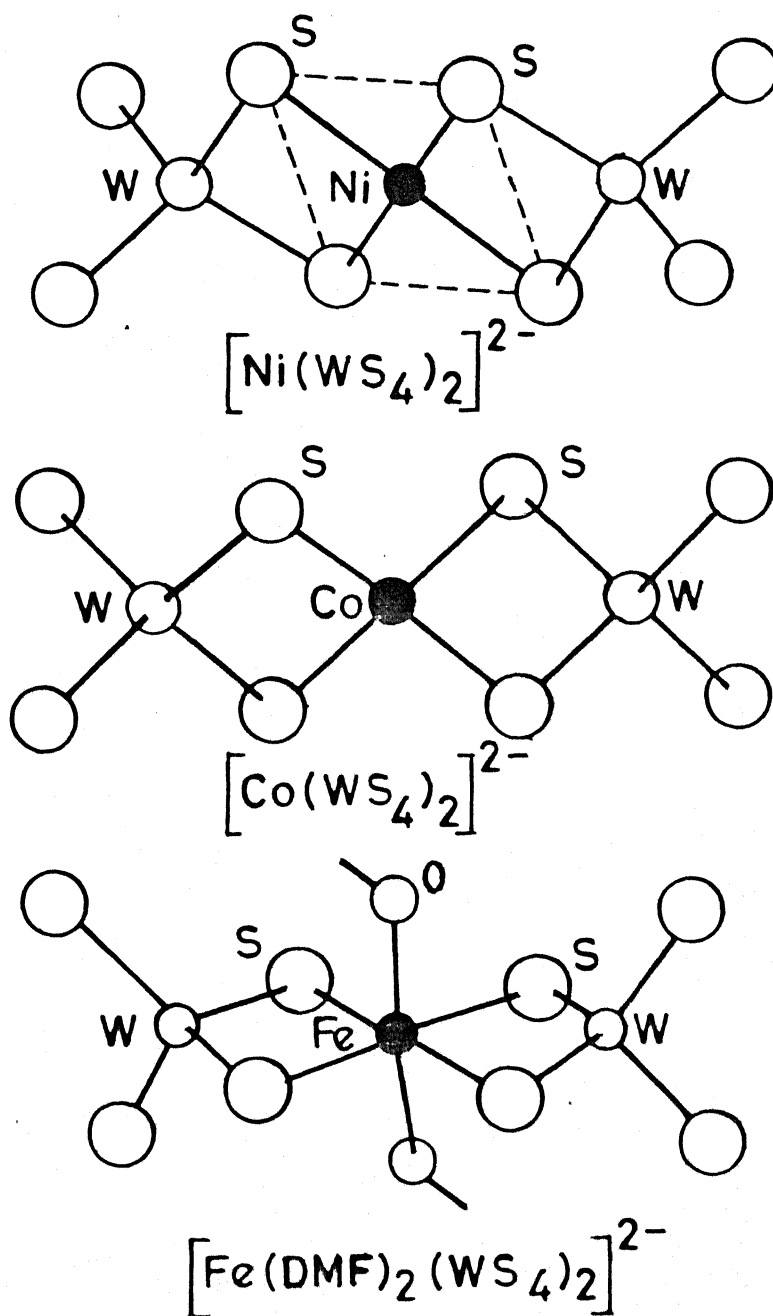
The following points have been observed in the above reactions.

- i) Bulky cations are essential to trap the dinegative complex anions [59].
- ii) When thiomolybdates are used, in addition to complex formation there is also the formation of amorphous products which necessitates purification steps [61].
- iii) The central metal is tetracoordinated and the coordination is always through the sulfur ends in all the cases [62,63].

- iv) The combination $M'=Fe$ and $M=Mo$ does not form any discrete bis(thiometallato) complex [65].
- v) Depending upon the nature of the central metal atom there can be squareplanar or tetrahedral arrangement of sulfur atoms around the heterometal. Thus the bis(thiometallato) complexes of $Ni(II)$ [67], $Pd(II)$ and $Pt(II)$ [66], are squareplanar while those of $Fe(II)$, $Co(II)$, [68] and $Zn(II)$ [69] are tetrahedral.

The reaction of ferrous salts with thiomolybdates in the presence of tetraphenylphosphonium ion in water leads to the formation of the polymeric species of approximate composition $(PPh_4)_2[Fe(MoS_4)_2]$ [65]. The tungsten analog viz., $[Fe(WS_4)_2]^{2-}$ can be prepared as a green paramagnetic ($S=2$), microcrystalline solid in analytically pure form [65]. The instability of the $[Fe(MoS_4)_2]^{2-}$ dianion can be explained on the basis of the base adduct forming tendencies of the analogous tetrathiotungstate complex. Such tendencies may cause rapid polymerization of the complex.

In coordinating solvents like DMF, DMSO or pyridine the $[Fe(WS_4)_2]^{2-}$ complex anion forms base adducts of the type $[Fe(WS_4)_2(DMF)_2]^{2-}$ [70]. $Fe(II)$ has an octahedral coordination in the above complex having two bidentate $[WS_4]^{2-}$ ligands and two DMF molecules in trans arrangement. Structures of squareplanar, tetrahedral and octahedral complexes having thiometallate ligands are presented in Fig. 1.2 .



SQUARE PLANAR, TETRAHEDRAL AND OCTAHEDRAL
STRUCTURES OF COMPLEXES WITH $(WS_4)^{2-}$
LIGANDS

FIG. 1.2

Complexes with different stoichiometries of the central metal and thiometallates also exist in addition to these simple 1:2 complexes (Table 1.2). The 2:4 complex anion $[\text{Sn}_2(\text{WS}_4)_4]^{4-}$ [71] demonstrates the tridentate nature of the thiometallates. In $[\text{Sn}_2(\text{WS}_4)_4]^{4-}$ two of the tetrathiotungstates are tridentate while the other two are bidentate. The 2:2 complex $[\text{Au}_2(\text{WS}_4)_2]^{2-}$ [72] has also been reported. In the 2:1 complex $[(\text{PPh}_3)\text{AgS}]_2\text{MS}_2$ ($\text{M}=\text{Mo}, \text{W}$) each heterometal is coordinated to one sulfur [73].

1.6 Iron-thiometallate complexes:

The synthesis and characterization of iron-thiometallate $[\text{Fe-M-S}]$ ($\text{M}=\text{Mo}, \text{W}$) complexes as structural models for the molybdenum site of nitrogenase has been the subject of intense investigations of many researchers. The chemistry of $[\text{Fe-M-S}]$ complexes derived from $[\text{MS}_4]^{2-}$ anions ($\text{M}=\text{Mo}, \text{W}$) has been reviewed by Coucouvanis [74] and Averill [75]. The importance of $[\text{Fe-M-S}]$ complexes in bioinorganic chemistry stems from the following observations.

- i) The iron-molybdenum cofactor (Fe-Mo-co) isolated from the Fe-Mo component protein of nitrogenase consists of approximately 2 molybdenums, 28-32 irons and 30 acid labile sulfurs [76].
- ii) The molybdenum K-edge EXAFS analysis of the Fe-Mo-co has shown the presence of a unique $[\text{Fe-Mo-S}]$ aggregate with four or five sulfur atoms around the molybdenum as well as two or three iron atoms in the second coordination sphere [77,78].

Table 1.2

Complexes of the type $[L(M')_x(MS_4)_y]^{n-}$
with different stoichiometries of the
central metal and thiometallate

Complex ion	Number x : y	N _s	N _b	Ref
$[Ni(WS_4)_2]^{2-}$	1 : 2	2	2	59
$[Fe(WS_4)_2]^{2-}$	1 : 2	2	2	65
$[Cl_2FeMS_4]^{2-}$	1 : 1	2	2	106
$[(FeCl_2)_2MS_4]^{2-}$	2 : 1	4	4	109
$[Fe_2S_2(MoO_2S_2)_2]^{4-}$	2 : 2	2	2	118
$[Fe_2S_2(WS_4)_2]^{4-}$	2 : 2	2	2	119
$[Fe_3S_2(WS_4)_3]^{4-}$	3 : 3	2	2	120
$[CNCuMoS_4]^{2-}$	1 : 1	2	2	12
$[Sn_2(WS_4)_4]^{4-}$	2 : 4	2 3	2 4	71
$[Au_2(WS_4)_2]^{2-}$	2 : 2	2	2	72
$[(PPh_3)_2Ag_2MS_4]$	2 : 1	2	2	73
$[Ru(bipy)_2MoS_4]$	1 : 1	2	2	130
$[Ru_2(bipy)_4MoS_4]^{2+}$	2 : 1	4	4	130
$[Rh_2(COD)_2WS_4]$	2 : 1	4	4	131
$[SW(WS_4)_2]^{2-}$	1 : 2	2	2	47
$[W(WS_4)_2]^{2-}$	1 : 2	2	2	53

M' = heterometal; M = Mo, W; L = coligand.

(bipy) = 2,2'-bipyridine; COD = 1,5-cyclooctadiene.

N_s = Number of coordinating sulfur atoms per thiometallate.

N_b = Number of M'—S bonds formed per thiometallate ligand.

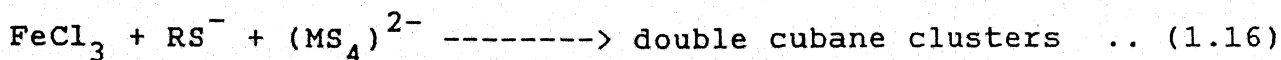
iii) Based on the EXAFS studies, several structures have been proposed for the Mo site of nitrogenase [78]. The proposed model structures ranging from a simple linear model to the novel cubane model for the molybdenum site of nitrogenase are presented in Fig. 1.3 .

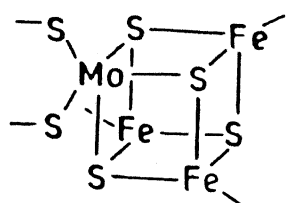
iv) The acid hydrolysis of the Mo-Fe protein produces a mixture of tetrathiomolybdate and oxotriithiomolybdate [79].

A number of [Fe-M-S] (Mo,W) complexes have been synthesized in recent years as possible models for the molybdenum site of the enzyme nitrogenase. These model complexes can be classified into two categories i) the cubane models and ii) the linear models. In all the model complexes synthesized till date, $[\text{MoS}_4]^{2-}$ has been used as the molybdenum source, since $[\text{MoS}_4]^{2-}$ is unique in providing a soluble, reactive source of molybdenum and sulfur, which can form complexes with iron salts. The choice of $[\text{MoS}_4]^{2-}$ as the starting material is also due to Zumft's observation [78] that $[\text{MoS}_4]^{2-}$ is one of the acid hydrolysis products of the enzyme. The analogous tungsten complexes have also been prepared for a comparative study.

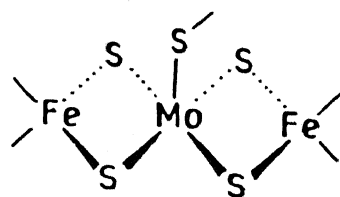
1.6.1 Cubane Models:

Most of the investigations on the cubane model compounds have been carried out by Holm and coworkers [80-90] and Garner and coworkers [91-100]. The "self assembly" of the double cubane clusters has been achieved by the reaction of ferric chloride with alkyl or aryl thiolates and tetrathiometallates in alcoholic solvents, which can be written as follows:

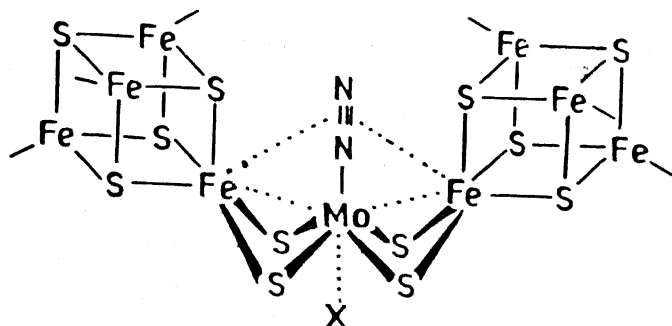




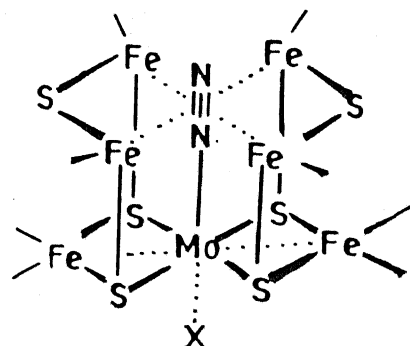
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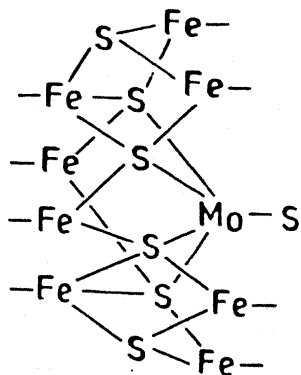
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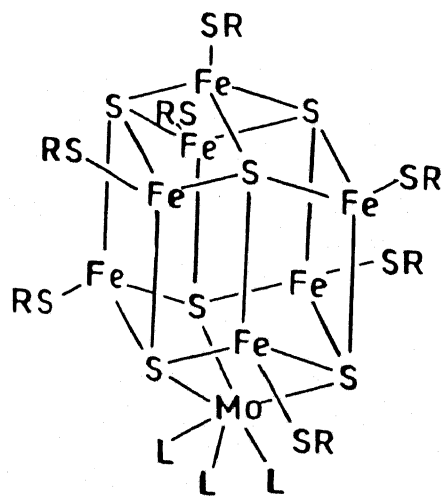
III



IV



V



VI

RECENT PROPOSALS FOR THE STRUCTURE OF THE
NITROGENASE MOLYBDENUM SITE

FIG. 1.3

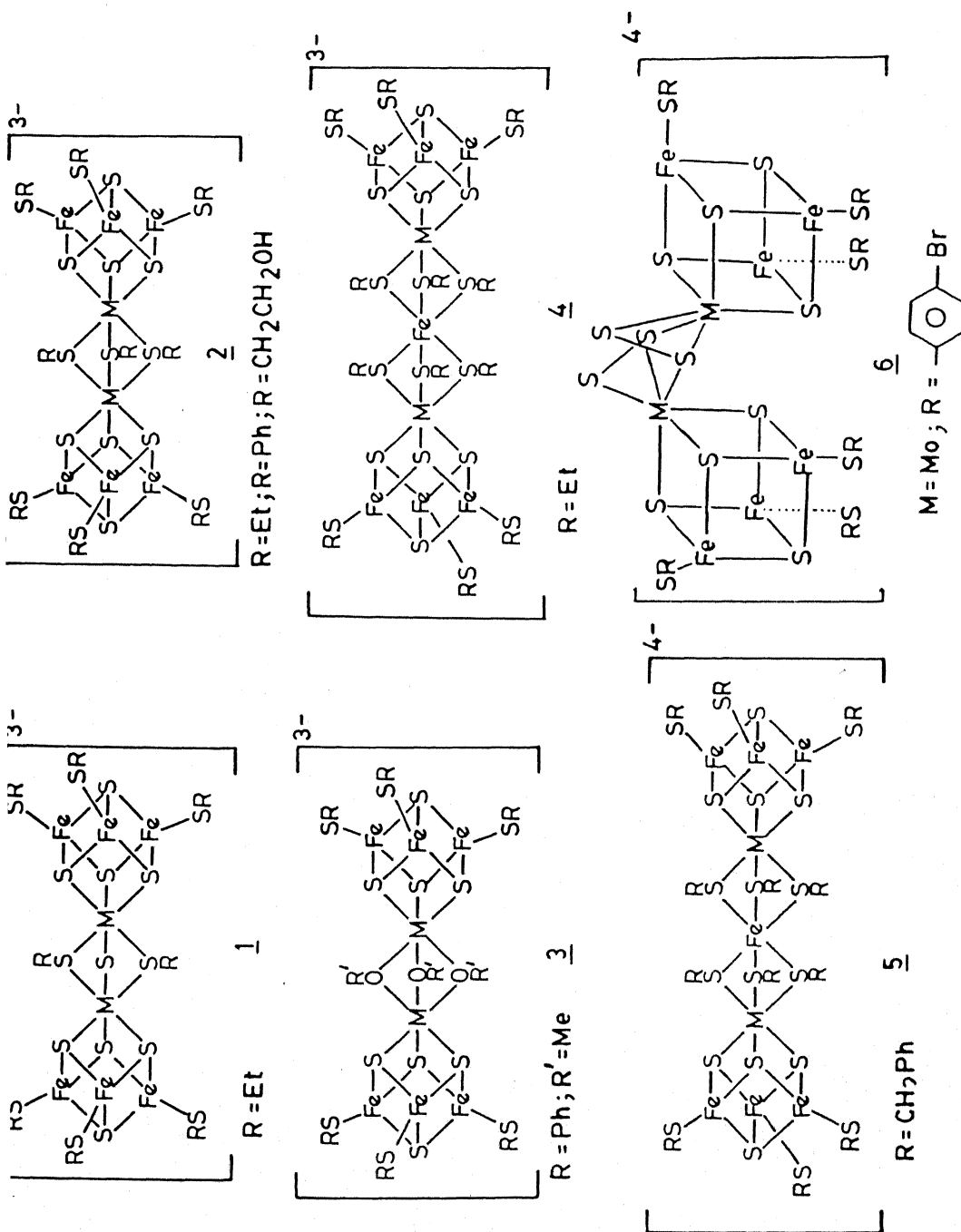
Six distinct types of anionic double cubane clusters have been prepared till date from the "self assembly" reactions of Fe^{3+} , RS^- and $[\text{MS}_4]^{2-}$ ($\text{M}=\text{Mo}, \text{W}$). They are as follows:

$[\text{M}_2\text{Fe}_6\text{S}_9(\text{SR})_8]^{3-}$, 1 [81-83]; $[\text{M}_2\text{Fe}_6\text{S}_8(\text{SR})_9]^{3-}$, 2 [91-93];
 $[\text{M}_2\text{Fe}_6\text{S}_8(\text{SR})_6(\text{OR}')_3]^{3-}$, 3 [93-94]; $[\text{M}_2\text{Fe}_7\text{S}_8(\text{SR})_{12}]^{3-}$, 4 [83-85];
 $[\text{M}_2\text{Fe}_7\text{S}_8(\text{SR})_{12}]^{4-}$, 5 [83-85]; $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{S}_2)_2(\text{SR})_6]^{4-}$, 6 [89];

The structures of the different types of double cubane clusters are shown in Fig. 1.4. The isolation of a particular product depends upon the nature of the substituent R, the choice of $\text{M} = \text{Mo}$ or W , solvent, reaction time, cation and ratio of iron and thiolate to tetrathiometalate.

All of these products of "self assembly" reactions contain two $\{\text{MFe}_3\text{S}_4\}$ cubes connected by a variety of bridging groups. The double cubanes 1, 2 and 3 differ only in the nature of the three groups connecting the molybdenum or tungsten atoms having one sulfide and two mercaptide, three mercaptide and three alkoxide bridging ligands respectively. The double cubanes 4 and 5 differ in having an additional ferric or ferrous iron and three mercaptide ligands inserted between the $\{\text{MFe}_3\text{S}_4\}$ cubes of 2. The double cubane 6 has two persulfido groups bridging the $\{\text{MoFe}_3\text{S}_4\}$ cubes.

The reaction of the $\text{Fe}(\text{III})$ bridged double cubane cluster 4 with excess of catechol, results in the smooth cleavage of the double cubane to afford the "catechol-capped" complex containing a single $\{\text{MoFe}_3\text{S}_4\}$ core, $[\text{MoFe}_3\text{S}_4(\text{SEt})_3\text{Fe}(\text{C}_6\text{H}_4\text{O}_2)_3]^{3-}$. This mono cubane complex consists of a $\{\text{MoFe}_3\text{S}_4\}$ cube to the molybdenum atom of which a tris(catecholate)iron(III) complex is attached via three bridging catecholate oxygens [86].



SCHEMATIC OF THE STRUCTURALLY CHARACTERIZED MoFe_3S_4 DOUBLE CUBANE CLUSTERS.

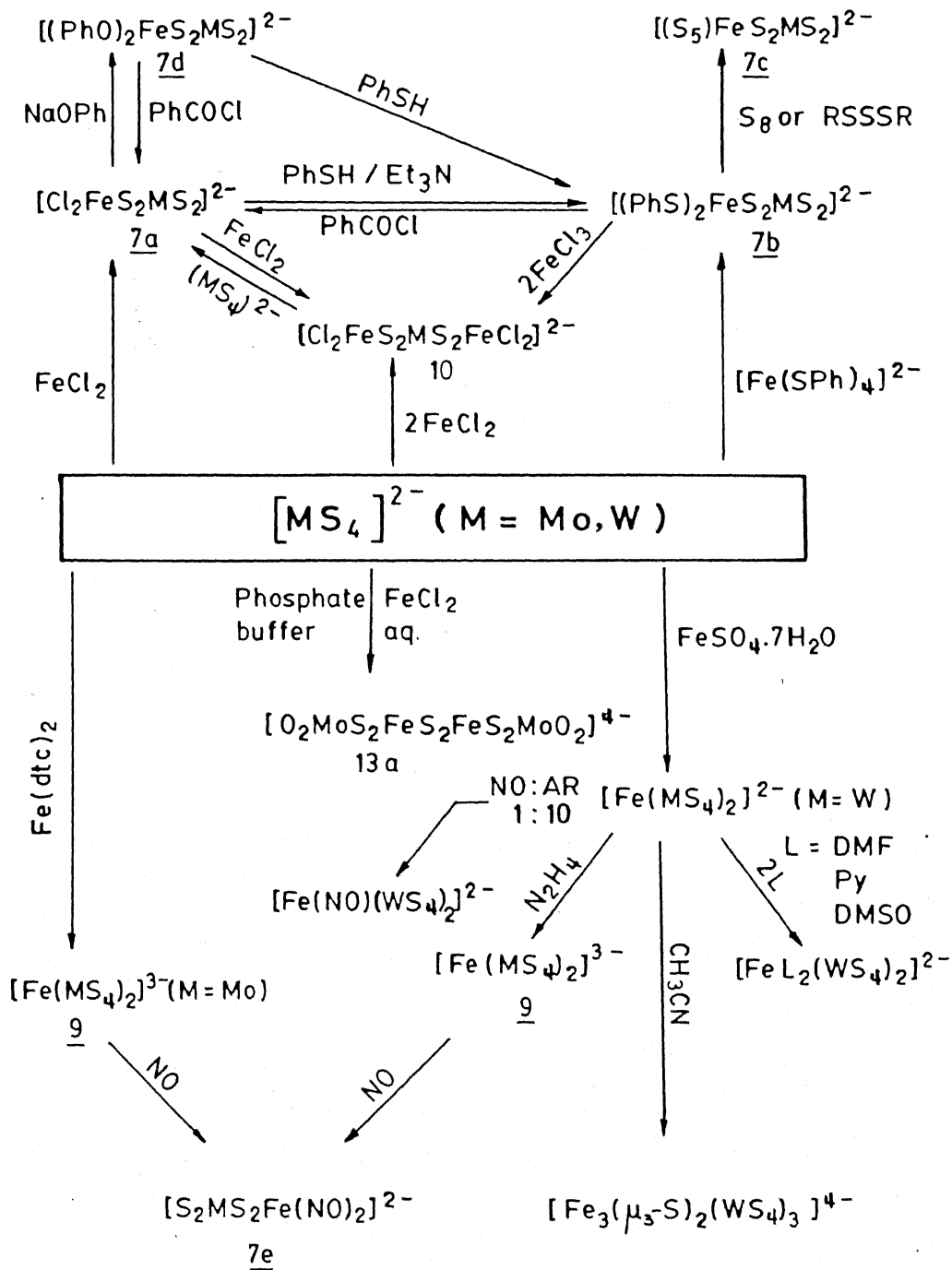
FIG.1.4

1.6.2 Linear [Fe-M-S] clusters:

All the linear [Fe-M-S] clusters have the unit $\{\text{Fe}(\mu\text{-S})_2\text{M}\}$ (M=Mo,W) in common and are generally synthesized by the reactions of ferrous sources of iron with thiometallates. Linear [Fe-M-S] clusters with various stoichiometries of iron and M (M = Mo, W) have been synthesized and structurally characterized. The syntheses of the different types of linear [Fe-M-S] clusters is presented in Scheme 1.

The 1:2 complex $[\text{Fe}(\text{MoS}_4)_2]^{3-}$ **9** is obtained readily by the reaction of $[\text{MoS}_4]^{2-}$ with iron xanthate or dithiocarbamate in dichloromethane [101-103]. It is one electron more reduced than the typical trinuclear $[\text{M}'(\text{MS}_4)_2]^{2-}$ clusters. The mechanism of the reduction is not clearly understood. The magnetic behavior of **9** has been studied and the complex has been formulated as a Fe(I) complex coordinated to two $[\text{MoS}_4]^{2-}$ ligands [104]. The reaction of NO with **9** does not give the expected NO adduct at the central iron, but results in the cleavage of one of the $[\text{MoS}_4]^{2-}$ units to give the mixed ligand complex $[\text{Fe}(\text{NO})_2\text{MoS}_4]^{2-}$ **7e** [105].

The complexes $[\text{FeCl}_2(\text{MS}_4)]^{2-}$ **7a** (106-108), $[(\text{FeCl}_2)_2\text{MS}_4]^{2-}$ **10** [109,110] are prepared simply by the reactions of $[\text{MS}_4]^{2-}$ with one or two equivalents of FeCl_2 respectively. The reaction of anhydrous ferrous acetate with $[\text{MS}_4]^{2-}$ results in the formation of the 1:1 complex $[(\text{AcO})_2\text{FeMS}_4]^{2-}$ **7f** [111]. The trinuclear complex **10** dissociates slowly in solvents like DMF to FeCl_2 and **7a** clearly indicating that the coordinated tetrathiometallate has very low affinity for a second metal ion [109].



THE $(MS_4)^{2-}$ THIOANIONS AS LIGANDS IN THE SYNTHESIS OF LINEAR Fe-M-S CLUSTERS

SCHEME -1

The complex $[\text{FeCl}_2(\text{MS}_4)]^{2-}$ **7a** undergoes many ligand exchange reactions. **7a** reacts with NaSPh leading to the formation of $[(\text{SPh})_2\text{FeMS}_4]^{2-}$ **7b** [106] which has also been obtained from the reaction of $[\text{Fe}(\text{SPh})_4]^{2-}$ with $[\text{MS}_4]^{2-}$ [112]. The novel sulfur ring complex $[(\text{S}_5)\text{FeMS}_4]^{2-}$ **7c** is obtained by reacting **7b** with organic trisulfides [113]. The chloride ligands in **7a** can also be exchanged with phenoxide ligands to yield the complex $[(\text{PhO})_2\text{FeMS}_4]^{2-}$ **7d** [114]. The reaction of **7d** with acyl chloride or thiophenol produces **7a** and **7b** respectively. All the ligand exchange reactions are quantitative indicating that $\{\text{Mo}(\mu\text{-S})_2\text{Fe}\}$ core is inert under these conditions [106].

The trinuclear clusters $[\text{S}_2\text{MS}_2\text{FeS}_2\text{Fe}(\text{SAr})_2]^{3-}$ **11** ($\text{Ar}=\text{Ph}$) are synthesized by the reaction of $[\text{MoS}_4]^{2-}$ with either $[\text{Fe}_2\text{S}_2(\text{SAr})_4]^{2-}$ or $[\text{Fe}_4\text{S}_4(\text{SAr})_4]^{2-}$ [115], while the trinuclear cluster $[(\text{RS})_2\text{MoS}_3\text{FeS}_3\text{Mo}(\text{SR})_2]^{3-}$ **12** is synthesized from an ill-defined mixture containing FeCl_3 , $[\text{MoS}_4]^{2-}$ and excess ethane-1,2-dithiolate [116]. The complex $[(\text{S}_2)(\text{O})\text{MoS}_2\text{FeCl}_2]^{2-}$ **8** having terminal oxo, disulfido, bridging sulfido ligands is obtained by the reaction of Cs_2MoOS_3 with FeCl_2 and elemental sulfur [117].

The tetranuclear complex, $(\text{PPh}_4)_4[(\text{MoO}_2\text{S}_2)_2\text{Fe}_2\text{S}_2]$, **13a** has been recently prepared by an aqueous reaction of FeCl_2 with either Cs_2MoOS_3 or $[\text{MoS}_4]^{2-}$ in the presence of phosphate buffer ($\text{pH}=12$). This reaction clearly indicates that $\text{Fe}(\text{II})$ accelerates the hydrolysis of $[\text{MoS}_{4-n}\text{O}_n]^{2-}$ anions. The tetranuclear W complex $[(\text{WS}_4)_2\text{Fe}_2\text{S}_2]^{4-}$, **13b**, with fully reduced $\{\text{Fe}_2\text{S}_2\}$ core is obtained by the reaction of $[\text{Cl}_2\text{FeWS}_4]^{2-}$ with NaHS [119].

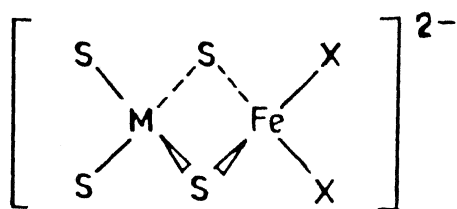
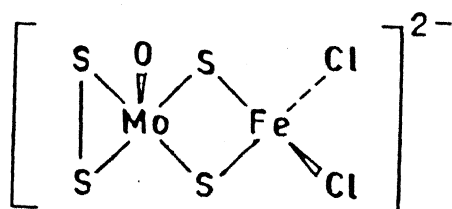
The novel hexanuclear cluster, $[\text{Fe}_3(\mu_3\text{-S})_2(\text{WS}_4)_3]^{4-}$, having a central $\{\text{Fe}_3(\mu_3\text{-S})_2\}$ moiety, is formed from acetonitrile solutions of $[\text{Fe}(\text{WS}_4)_2]^{2-}$ in good yields [120]. The three iron atoms of the central unit form an equilateral triangle having one each of $(\mu_3\text{-S})^{2-}$ ligand above and below this plane. Each Fe atom is bidentately coordinated by a $[\text{WS}_4]^{2-}$ ligand. The structures of some linear $[\text{Fe-M-S}]$ ($\text{M}=\text{Mo}, \text{W}$) complexes are presented in Fig 1.5.

Single crystals of the enzyme nitrogenase have been recently examined by EXAFS [121]. For comparison the double cubane complex $[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SEt})_9]^{3-}$ and the linear complex $[(\text{FeCl}_2)_2\text{MoS}_4]^{2-}$ were also examined. It has been concluded from these studies that none of the $[\text{Fe-M-S}]$ clusters synthesized so far, are compatible with the enzyme. The field is still open to researchers for the synthesis of the ultimate model complex.

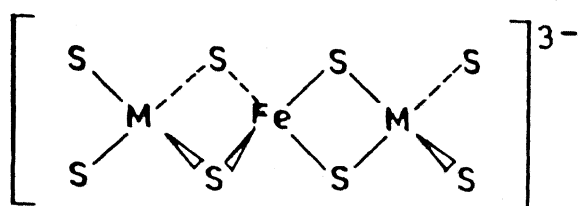
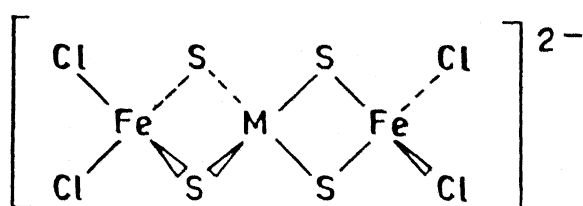
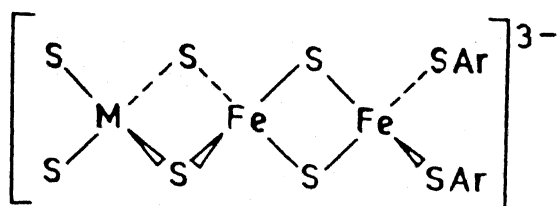
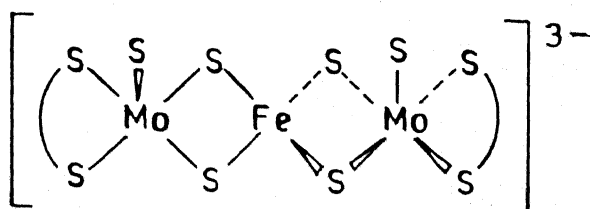
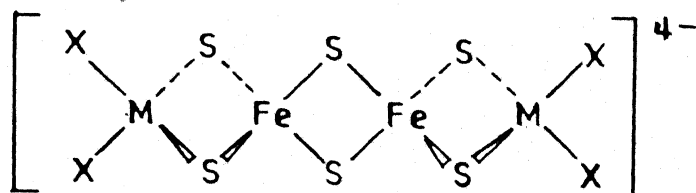
1.7 Thiometallate complexes of cobalt and nickel:

The interest in the thiometallate complexes of Co and Ni is mainly due to the relevance of $[\text{M}'\text{-M-S}]$ ($\text{M}'=\text{Co}, \text{Ni}$) systems in hydrodesulfurization (HDS) catalysts. It has been reported that the decomposition products of Co and Ni thiometallates act as excellent hydrodesulfurization catalysts [123]. There are only a few complexes reported in the literature, which are mostly bis-(thiometallato) complexes [60-63].

The bis(thiometallato) complexes of cobalt $[\text{Co}(\text{MS}_4)_2]^{2-}$ exhibit strong electron delocalization between metal centers of different valence states. The enormous decrease in electron density at the cobalt center, as in $[\text{Co}(\text{WS}_4)_2]^{2-}$, makes it possible to reduce this species easily or add a free ligand like NO.

78

- a. (X = Cl) d. (X = OPh)
 b. (X = SPh) e. (X = NO)
 c. (X₂ = S₅) f. (X = OAC)

910111213

- a. M = Mo, X = O ; b. M = W, X = S

SCHEMATIC OF THE STRUCTURALLY CHARACTERIZED
 LINEAR Fe -M-S CLUSTERS

Thus the mixed ligand complex $[\text{Co}(\text{NO})(\text{WS}_4)_2]^{2-}$ [65] is readily obtained by a simple reaction of $[\text{Co}(\text{WS}_4)_2]^{2-}$ with NO diluted in argon (1:10). However, prolonged passage of gaseous NO leads to the cleavage of one of the $[\text{WS}_4]^{2-}$ units resulting in the formation of the dinitrosyl complex $[\text{Co}(\text{NO})_2\text{WS}_4]$. The reduction of the dinegative bis(thiometallato) cobalt complexes with sodium borohydride yields the trianions $[\text{Co}(\text{MS}_4)_2]^{3-}$ [124].

The attempted synthesis of the cobalt complexes analogous to $[\text{FeCl}_2(\text{MS}_4)]^{2-}$, from anhydrous CoCl_2 and thiometallates in non-aqueous solvents does not result in the formation of 1:1 complexes but gives exclusively bis(thiometallate) complexes [124]. This has been attributed to the existence of CoCl_2 as completely solvated Co^{2+} unlike FeCl_2 where the integrity of the Fe-Cl linkage is maintained [124].

The nickel thiometallate chemistry is very much unexplored. But for the squareplanar bis(thiometallato)nickel complexes of the type $[\text{Ni}(\text{MS}_{4-n}\text{O}_n)_2]^{2-}$ ($\text{M}=\text{Mo}, \text{W}; n=0-2$) no other complexes are known [59-63]. The thermal decomposition product of $[\text{Ni}(\text{WS}_4)_2]^{2-}$ acts as a good HDS catalyst [123]. Of late there has been some interest in [Ni-M-S] chemistry to synthesize Ni-thiometallate complexes which can be precursors to HDS catalysts.

The attempted synthesis of $[\text{Cl}_2\text{Ni}(\text{MS}_4)]^{2-}$ by the reaction of either NiCl_2 or $[(\text{PPh}_3)_2\text{NiCl}_2]$ with $[\text{MS}_4]^{2-}$ in DMF yields only $[\text{Ni}(\text{MS}_4)_2]^{2-}$ clearly indicating the facile formation of the squareplanar bis(thiometallate) complex to the presence of NiCl_2 as only Ni^{2+} in the reaction medium [125].

1.8 Thiometallate complexes of copper:

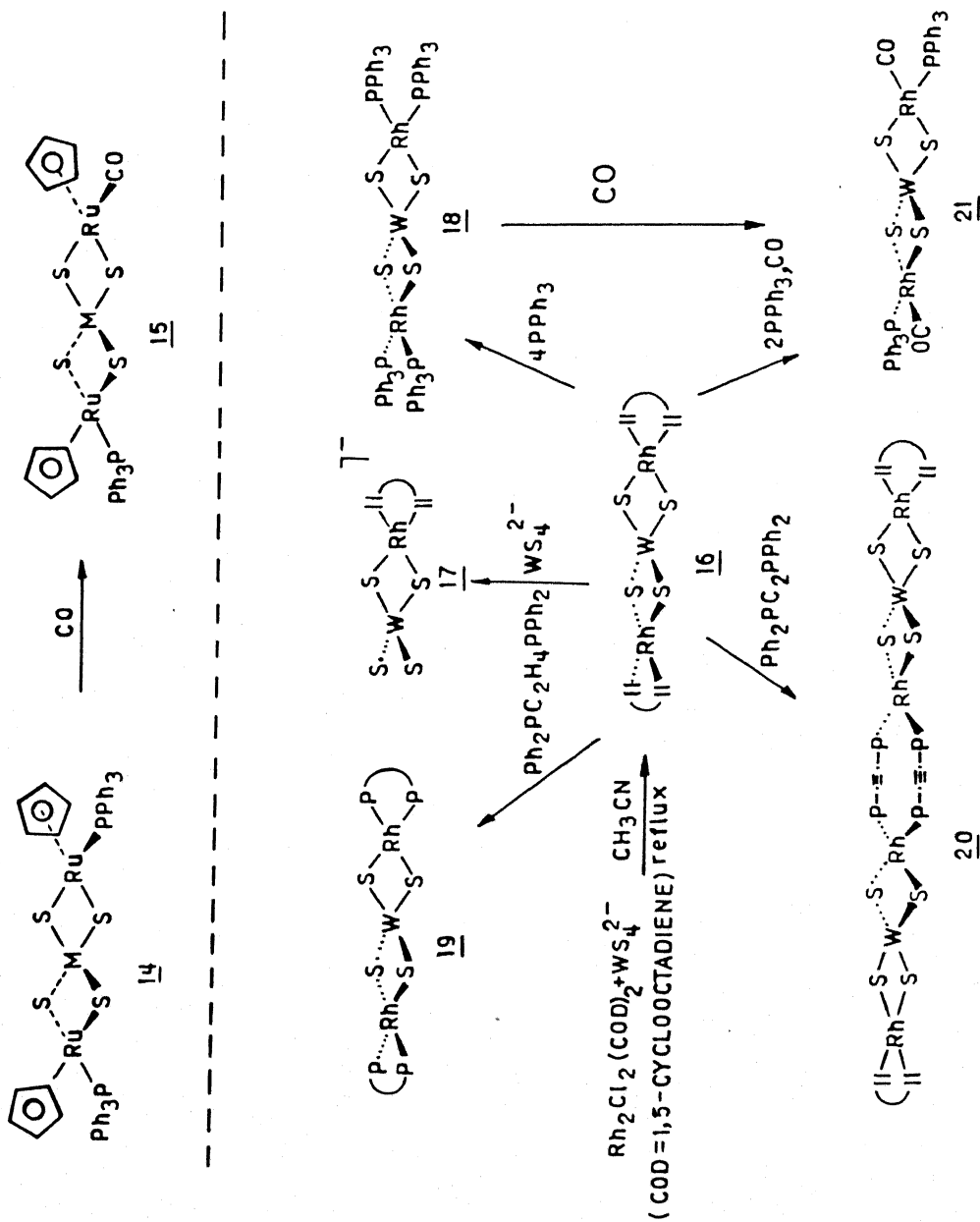
The aqueous reaction of cupric salts with $(\text{NH}_4)_2\text{MoS}_4$ results in the reduction of cupric to cuprous and the formation of a polymeric species $\text{NH}_4\text{CuMoS}_4$ [126]. These polymeric Cu-Mo compounds consist of chains of CuS_4^- and MoS_4^- tetrahedra connected via the edges. The polymerization of the above copper thio-metallate system can be inhibited by the presence of N- and P-donor ligands at the copper site. This strategy has been used and a number of mixed ligand complexes of copper have been synthesized and studied by various physical methods [127,128]. The Cu-thiometallate chemistry has been studied in detail in an effort to understand the chemical implications of Cu-Mo antagonism and has been reviewed recently by Sarkar and Mishra [129].

1.9 Thiometallate complexes of 4d and 5d metals:

The chemistry of the thiometallate complexes of 4d and 5d metals has not been studied in detail. In fact, very little work has been done in this area. The squareplanar bis(thiometallato) complexes of Pd and Pt are well known [66].

The reaction of $[\text{Ru}(\text{bipy})_2\text{Cl}_2]$ with tetrathiomolybdate yields the neutral mixed ligand complex $(\text{bipy})_2\text{RuMoS}_4$ [130]. The reaction of the dinuclear complex $[(\text{bipy})_2\text{RuMoS}_4]$ further with $[\text{Ru}(\text{bipy})\text{Cl}_2]$ results in the formation of an air-sensitive cationic complex $[(\text{bipy})_2\text{RuS}_2\text{MoS}_2\text{Ru}(\text{bipy})_2]^{2+}$.

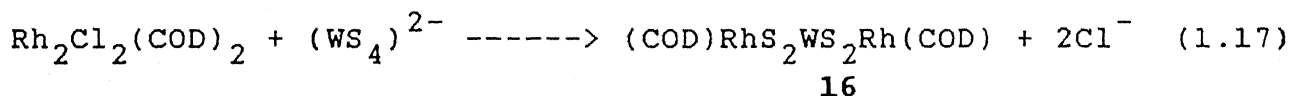
The chemistry of the thiometallates with organometallic complexes of ruthenium and rhodium has been studied by Rauchfuss and coworkers [131]. The reaction of thiometallates with organometallic complexes is presented in Scheme 2.



SCHEME - 2

In the reaction of $(RC_5H_4)Ru(PPh_3)_2Cl$ ($R=H, CH_3$) with $[MS_4]^{2-}$ the thiometallate acts as a two-fold bidentate ligand to yield the 2:1 complex $[(RC_5H_4)Ru(PPh_3)_2]MS_4$ ($M=Mo, W$). All the four sulfur atoms are bridging in 14. The trinuclear complex 14 reacts rapidly with CO to give the monocarbonyl complex 15, wherein, one of the PPh_3 of 14 has been exchanged for CO.

The reaction of $(Ph_4P)_2WS_4$ with $[Rh(COD)Cl]_2$ (COD=1,5-cyclooctadiene) results in the formation of the trinuclear complex 16 as given in eq. (1.17)



When excess of $(WS_4)^{2-}$ is used the 2:1 complex 16 yields the dinuclear complex 17. The trinuclear complex 16 undergoes ligand substitution reactions (Scheme 2) with triphenylphosphine, 1,2-bis(diphenylphosphino)ethane to give 18 and 19 respectively. The complex 16 reacts with 1,2-bis(diphenylphosphino)acetylene to give the spectacular hexanuclear species 20. The carbonyl complex 21 has also been prepared by the reaction of 16 with CO in the presence of PPh_3 . The above reactions are summarized in Scheme 2. The synthesis of $(As_4S_{14}Mo_2O_2)$ from the reaction of $[MoS_4]^{2-}$ with As_4S_4 has also been reported by Rauchfuss and coworkers, which adds a new dimension to thiometallate chemistry [132].

1.10 Spectroscopic investigations:

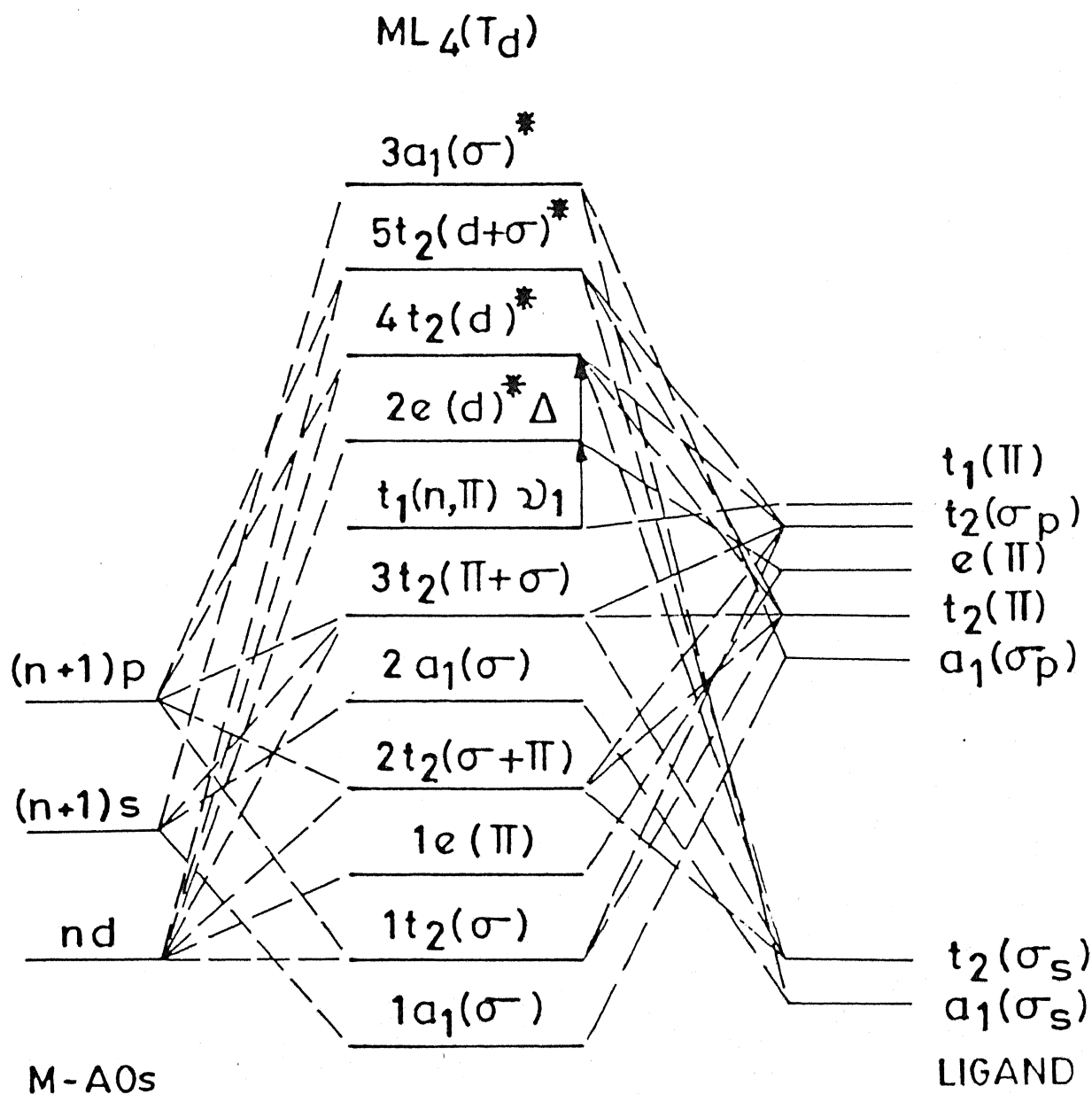
The free thiometallates and the coordinated thiometallates have been studied by a variety of physical methods and useful information on the structure, the nature of the chemical bonding and stability of these compounds has been obtained. The results of these investigations are presented below.

1.10.1 Electronic spectroscopy:

The simple thiometallates have characteristic high intensity absorption bands in the uv-visible region. The first indication of the type of bonding is given by the metal-sulfur bond lengths which are significantly shorter than the sum of the ionic or covalent radii and thus suggest a bond order > 1 i.e. the involvement of π -bonds [20-22]. The Mo-S bond length in $[\text{MoS}_4]^{2-}$ or $[\text{MoOS}_3]^{2-}$ lies between those for a double and single bonds. The involvement of π -bonding is also demonstrated by various physical measurements [133-136] and by MO-calculations.

The simplified molecular orbital diagram for $[\text{MS}_4]^{n-}$ ions with T_d symmetry is given in Fig. 1.6. The proportion of π -contributions in the respective metal-sulfur bonds of analogous species increases in the sequence $\text{V} < \text{Mo} < \text{W} < \text{Re}$. It is also appreciably higher compared to the thioanions of the main group elements [137].

Unambiguous assignment is only possible for the longest-wavelength band (ν_1) that is $t_1 \rightarrow 2e$ using magnetic circular dichroism measurements [138,139]. Assignments to the higher energy transitions ν_2, ν_3 are not straight forward. On the basis of empirical considerations the tentative assignments $\nu_2 = 3t_2 \rightarrow 2e$ and $\nu_3 = t_1 \rightarrow 4t_2$ have been made [139]. The longest wavelength band (ν_1) of the $[\text{MoOS}_3]^{2-}$ species can be unambiguously assigned to $(a_2 \rightarrow e)$ transitions since in the resonance Raman spectra only the intensities of the lines corresponding to vibrations in the MS_3 chromophores are enhanced [140]. The electronic spectral data of some thiometallates is presented in Table 1.3 [138].



Molecular orbital scheme for tetrahedral MS_4^{n-} ions.

FIG. 1-6

Table 1.3

Infrared and electronic spectral data
of some thiometallates [133,138]

Compound	Infrared (cm^{-1})		UV/Visible nm (ϵ)		
	$\nu(\text{MS})$	$\nu(\text{MO})$	ν_1	ν_2	ν_3
$(\text{NH}_4)_2\text{MoS}_4$	476	---	463(1.30)	316(1.80)	241(2.95)
$(\text{NH}_4)_2\text{WS}_4$	458	---	391(1.85)	276(2.85)	---
Cs_2MoOS_3	473	854	460(0.23)	392(0.87)	319(0.60)
Cs_2WOS_3	457	872	380(0.30)	330(1.13)	270(0.72)
$(\text{NH}_4)_2\text{MoO}_2\text{S}_2$	490	830,792	394(0.30)	319(0.6)	288(0.30)
$(\text{NH}_4)_2\text{WO}_2\text{S}_2$	470	850,795	327(0.40)	273(0.69)	244(0.39)
* $(\text{MoO}_3\text{S})^{2-}$	-	---	392	288	---
* $(\text{WO}_3\text{S})^{2-}$	-	---	327	244	---

ϵ values $\times 10^4$ in parentheses ($\text{l.mol}^{-1}.\text{cm}^{-1}$)

* exists only in solution

The electronic spectra of coordinated thiometallates are entirely different from that of the free thiometallates. Various physical measurements have demonstrated that in thiometallato complexes with central metal possessing open d-shells, there are strong metal-ligand interactions. The known complexes of the type $[M'(MS_{4-n}O_n)_2]^{2-}$ ($M = Mo, W$; $M' = Fe, Co, Ni, Pd, Pt$) show characteristic absorption bands whose positions are only roughly comparable to those in free thiometallates [12].

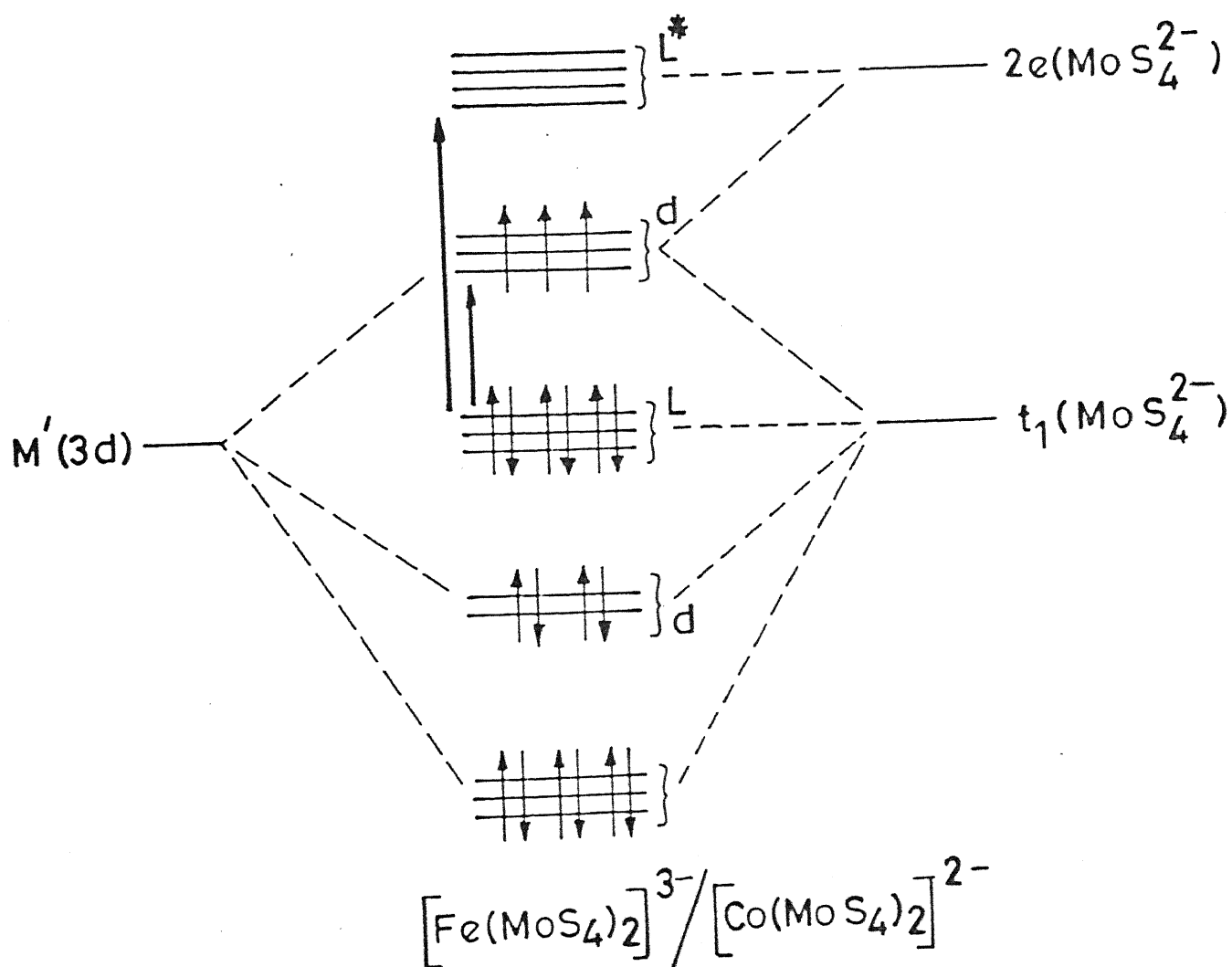
The reduction of the symmetry due to complex formation leads to the splitting of the bands. The spectra in the region of the ligand internal transitions depend markedly on the nature of the central metal because of strong $M'-L$ (L =thiometallate) interactions. Thus there is a characteristic splitting of the ν_1 band of the free $[WS_4]^{2-}$ in the $[Ni(WS_4)_2]^{2-}$ complex. Contrary to this, the longest-wavelength band in $[Ni(MoS_4)_2]^{2-}$ is strongly red shifted. This bathochromic shift suggests strong $d\pi(Ni)$ interactions with the ligand orbitals in $[Ni(MoS_4)_2]^{2-}$. This interaction is so strong that the complex can no longer be formulated as a $Ni(II)-Mo(VI)$ complex and one must think in terms of a formal reduction of the Ni center and a partial disulfide bond between the bridging S atoms. The bis(thiometallato) complexes of Fe and Co exhibit an intense band in the NIR-VIS region which can be assigned to charge-transfer transitions of the type $L \rightarrow d(M')$. The electronic spectra of the complexes of the type $[X_2FeS_2MS_2]^{2-}$ ($X = Cl, PhS, 1/2 S_5$) are very similar, where the $M'-L$ interaction is smaller than in the trimetallic complexes. The $[Fe-M-S]$ complexes show a broad absorption band

with considerable structure centered around 1000 nm which has been tentatively assigned to Fe-Mo(W) transitions by Coucouvanis [74].

The instability of the $[\text{Fe}(\text{MoS}_4)_2]^{2-}$ ion can be explained using a qualitative MO-scheme for the isoelectronic complexes $[\text{Fe}(\text{MoS}_4)_2]^{3-}$ and $[\text{Co}(\text{MoS}_4)_2]^{2-}$ as shown in Fig. 1.7. The low energy MO's of the $3d(\text{M}')$ type in the cobalt and iron complexes are situated at a lower energy and in the case of $[\text{Fe}(\text{WS}_4)_2]^{2-}$ at about the same energy. Thus the unstable discrete $[\text{Fe}(\text{MoS}_4)_2]^{2-}$ is stabilized by taking one electron to form $[\text{Fe}(\text{MoS}_4)_2]^{3-}$ and $[\text{Fe}(\text{WS}_4)_2]^{n-}$ exists with $n=2$ and 3 . The salient features of this molecular orbital description suggest the following:

- i. In these trinuclear complexes, the electron density on the M' center is diminished whereas that on the M center is increased relative to the free $[\text{MS}_4]^{2-}$.
- ii. The electron density on the terminal S atom is hardly altered by electron delocalization.
- iii. Delocalized molecular orbitals over the metal centers M' and M occur in the units $\{\text{M}'\text{S}_2\text{MS}_2\text{M}'\}$.

The electronic spectra of the complexes with d^{10} central metal atoms $[\text{Zn}(\text{II}), \text{Cu}(\text{I})]$ show essentially ligand internal transitions corresponding to those of the free thiometallate ions. Amongst the three ligand internal transitions the first (ν_1) and the third (ν_3) bands are changed in their structure by complex formation while the second (ν_2) band is practically unaltered in its position, intensity and half-width. The electronic spectral data of some thiometallato complexes are listed in Table 1.4.



Molecular orbital scheme for complexes of MS_4^{n-} ions with open - d shell elements.

FIG. 1.7

Table 1.4

Electronic spectral data of some thiometallato complexes [12,74]

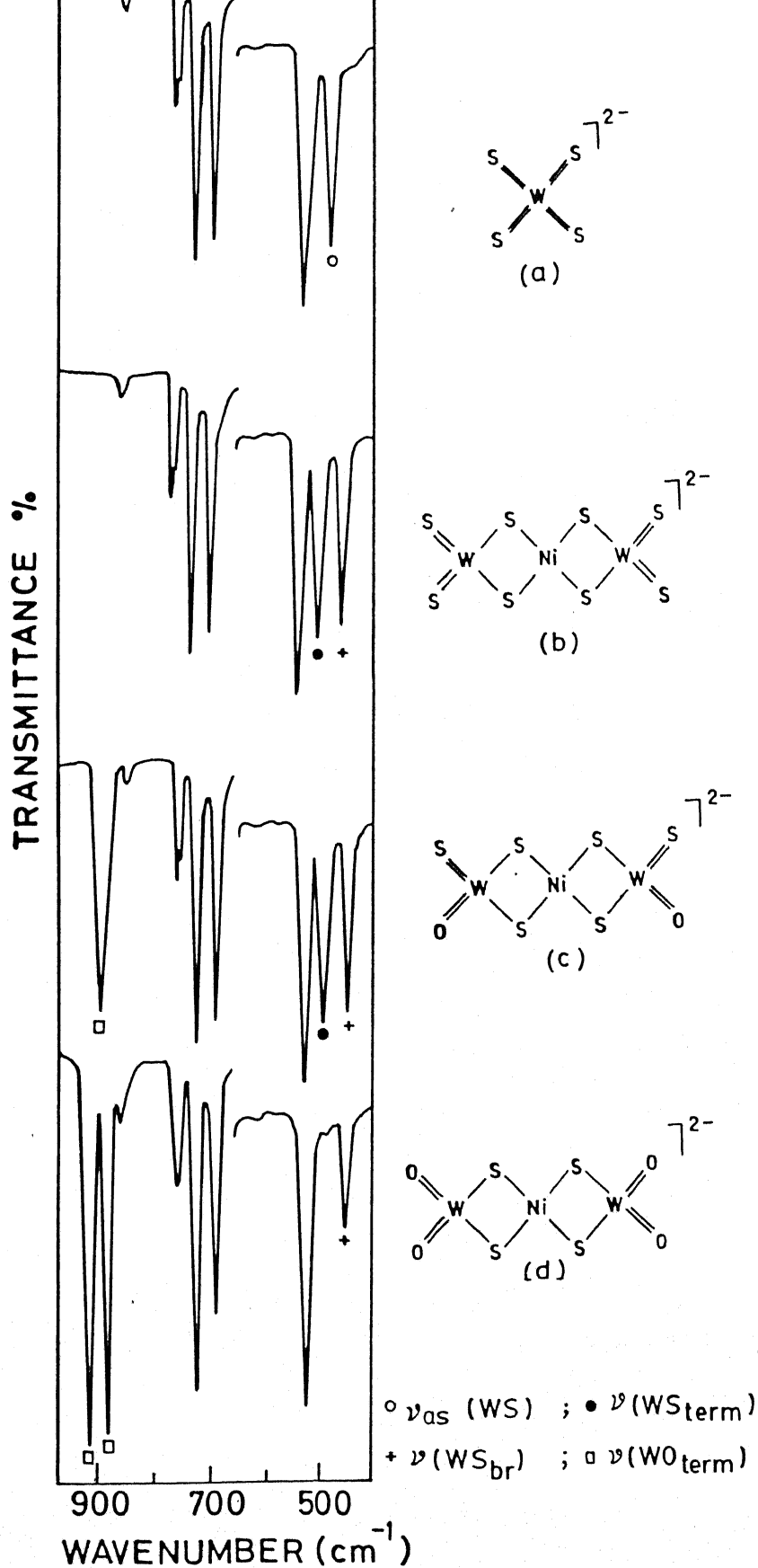
Complex	Color	Band Maxima (nm)
$[\text{Cl}_2\text{FeMoS}_4]^{2-}$	Dark brown	585, 521, 472, 435, 313, 285
$[\text{Fe}(\text{MoS}_4)_2]^{3-}$	Violet	629, 578, 507, 410
$[\text{Fe}(\text{WS}_4)_2]^{3-}$	Orange	555, 492, 434, 360
$[\text{Fe}(\text{WS}_4)_2]^{2-}$	Green	613, 426, 375
$[(\text{Cl}_2\text{Fe})_2\text{MoS}_4]^{2-}$	Brown	595, 565, 475, 399, 320
$[\text{Co}(\text{WS}_4)_2]^{2-}$	Olive-green	1163, 819, 387
$[\text{Co}(\text{WOS}_3)_2]^{2-}$	Olive-green	1205, 724, 367, 330
$[\text{Ni}(\text{MoS}_4)_2]^{2-}$	Dark brown	512, 395, 333
$[\text{Ni}(\text{WS}_4)_2]^{2-}$	Red brown	699, 420, 380
$[\text{Ni}(\text{MoOS}_3)_2]^{2-}$	Brown	458, 362, 322
$[\text{Ni}(\text{WOS}_3)_2]^{2-}$	Brown	683, 380, 332
$[\text{Pd}(\text{MoS}_4)_2]^{2-}$	Red	471, 383, 349, 316
$[\text{Pd}(\text{WS}_4)_2]^{2-}$	Brown-red	397, 367, 313
$[\text{Pt}(\text{MoS}_4)_2]^{2-}$	Red	513, 411, 363, 307
$[\text{Pt}(\text{WS}_4)_2]^{2-}$	Brown-orange	416, 312
$[\text{Zn}(\text{MoS}_4)_2]^{2-}$	Brown	571, 467, 313, 247, 233
$[\text{Zn}(\text{WS}_4)_2]^{2-}$	Orange	460, 395
$[\text{Cd}(\text{WS}_4)_2]^{2-}$	Orange	462, 395
$[\text{Hg}(\text{WS}_4)_2]^{2-}$	Orange	448, 395

1.10.2 Vibrational spectroscopy:

The vibrational spectroscopy has always been a powerful tool for the inorganic chemist which provides valuable structural information. The free thiometallates have characteristic $M=S$ and $M=O$ ($M=Mo, W$) stretching vibrations [$\nu(MS)$ 400-500 cm^{-1} ; $\nu(MO)$ 800-1000 cm^{-1}] in their infrared (IR) and Raman spectra. The vibrational analyses of many thiometallates have been done and the bands assigned [141,142]. The IR spectral data of some thiometallates are listed in Table 1.3 .

The vibrational spectra of many thiometallato complexes have been studied in detail and complete normal coordinate analyses have been performed on many bis(thiometallato) complexes by the isotope substitution technique. The structures of the complexes of the type $[M'(MS_4)_2]^{2-}$ predicted by a combination of vibrational analysis, electronic spectra and magnetic measurements [60,138,143-145] were later confirmed by single crystal X-ray structure analysis [67-69].

The vital proof for the bidentate nature and sulfur ligation of the thiometallate ligands can be obtained from a simple vibrational analysis. As a representative example, the IR analysis of the complex dianion $[Ni(WS_4)_2]^{2-}$ is discussed [143]. The IR spectra of the free and the coordinated $[WS_4]^{2-}$ is presented in Fig.1.8. In the free $[WS_4]^{2-}$ ion which has T_d symmetry, the IR active triply degenerate W-S stretch occurs at about 455 cm^{-1} and the Raman active totally symmetric stretch is at 479 cm^{-1} . Upon complexation the symmetry is reduced to C_{2v} and four bands are expected to appear in the IR spectrum with two bands increa-



INFRARED SPECTRA OF FREE (a) AND
COORDINATED THIOTUNGSTATE (b) - (d)

sing in frequency corresponding to $\nu(W=S_{\text{term}})$ and two bands decreasing in frequency corresponding to $\nu(W-S_{\text{br}})$. In agreement with this prediction, two closely spaced intense bands at 490 cm^{-1} and one broader intense band at 450 cm^{-1} are observed. In practice, the terminal M=S groups are characterized by one or two vibrational frequencies between $480\text{--}510 \text{ cm}^{-1}$ and the bridging M-S groups by frequencies between 430 and 460 cm^{-1} .

In the case of complexes of the type $[M'(MOS_3)_2]^{2-}$ [62], in addition to the characteristic stretching frequencies for the terminal M=S groups (νMS_{term}) and the bridging M-S groups (νMS_{br}) a band is observed for the terminal M=O group (νMO) (Fig.1.8 c). In complexes of the type $[M'(MO_2S_2)_2]^{2-}$ [63], the frequencies corresponding to terminal M=O groups and bridging M-S groups are only observed, indicating the preferential sulfur ligation of the thiometallate ligands (Fig 1.8). The IR spectrum of the polymeric complex $[Fe(MoS_4)_2]$ is conspicuous by the presence of broad unresolved bands in the $500\text{--}400 \text{ cm}^{-1}$ region unlike the other discrete thiometallato complexes [65]. The IR spectral data of some bis(thiometallato) complexes are listed in Table 1.5.

The ligand internal transitions in thiometallato complexes roughly correspond to those of the free thiometallates. Hence all the thiometallato complexes exhibit well resolved resonance Raman spectra. In these spectra the bands due to the totally symmetric vibrations of the $[MS_4]^{2-}$ chromophores are enhanced in intensity [110,146-148]. The resonance Raman effect can be used as a sensitive probe for the detection of $[MS_4]^{2-}$ ligands and to make distinction between the different modes of coordination (for e.g.

Table 1.5

Infrared spectral data of some bis(thiometallato) complexes

Complex	Infrared Data (cm ⁻¹)			Ref.
	$\nu(\text{MO}_{\text{term}})$	$\nu(\text{MS}_{\text{term}})$	$\nu(\text{MS}_{\text{br}})$	
[Fe(MoS ₄) ₂] ³⁻	---	495,472	438	101
[Fe(WS ₄) ₂] ³⁻	---	472	431	103
[Fe(WS ₄) ₂] ²⁻	---	493,484	450,438	65
[Co(WS ₄) ₂] ²⁻	---	500,491	450,442	60
[Co(WOS ₃) ₂] ²⁻	917,907	490,485	445	62
[Co(MoO ₂ S ₂) ₂] ²⁻	903,884	---	453,447	64
[Co(WO ₂ S ₂) ₂] ²⁻	927,892	---	---	63
[Ni(MoS ₄) ₂] ²⁻	---	505,483	445,434	61
[Ni(WS ₄) ₂] ²⁻	---	490,487	449,447	60
[Ni(MoOS ₃) ₂] ²⁻	896,884	500,492	458,446	64
[Ni(WOS ₃) ₂] ²⁻	921,908	496,486	450	62
[Ni(MoO ₂ S ₂) ₂] ²⁻	896,880	---	463,453	64
[Ni(WO ₂ S ₂) ₂] ²⁻	916,883	---	451	63
[Pd(MoS ₄) ₂] ²⁻	---	513,497	450,435	66
[Pd(WS ₄) ₂] ²⁻	---	499,491	440	66
[Pt(MoS ₄) ₂] ²⁻	---	510,496	454,433	66
[Pt(WS ₄) ₂] ²⁻	---	498,489	446,438	66
[Zn(MoS ₄) ₂] ²⁻	---	502,491	452,440 433	61
[Zn(WS ₄) ₂] ²⁻	---	489	446	60
[Cd(WS ₄) ₂] ²⁻	---	493,486	435	12
[Hg(WS ₄) ₂] ²⁻	---	493,486	431	12

whether two of the S atoms are bridging or all the four S atoms are bridging) of thiometallates. By using this technique the structure of the trinuclear complex $[(PPh_3)_2AgS_2MoS_2Ag(PPh_3)_2]$ for which single crystals could not be obtained, has been convincingly proved [146]. The complex in question shows a single strong symmetrical stretching vibration band and its overtones as expected from a local D_{2d} symmetry of the $\{AgS_2MoS_2Ag\}$ fragment. Hence in this trinuclear complex all the S atoms are bridged sulfurs. In contrast, the bidentate thiometallate shows bands characteristic of the totally symmetric vibrations of the terminal and bridging $\{MoS_2\}$ groups [148].

1.10.3 Magnetic resonance spectroscopy

Proton magnetic resonance spectroscopy has been used to check the purity of the double cubane clusters mentioned earlier. The RS^- ligands (R = alkyl or aryl) exhibit characteristic 1H NMR signals [75]. The advent of commercially available fourier transform spectrometers equipped with superconducting magnets has enabled the use of ^{95}Mo NMR as a sensitive probe to investigate the metal environment in molybdenum complexes. The ^{95}Mo resonances are characteristic of the oxidation state of the metal and its environment. The application of ^{95}Mo NMR to solve problems in inorganic chemistry and biochemistry is becoming popular and this field has been reviewed recently [149]. The ^{95}Mo NMR spectra of the nickel group bis(thiomolybdate) complexes have recently been reported [150]. The coordination of $[MoS_4]^{2-}$ to Ni(II), Pd(II) and Pt(II) results in an increased shielding of the Mo nucleus is indicated by ^{95}Mo chemical shifts.

The EPR spectrum of the complex $[\text{Fe}(\text{MoS}_4)_2]^{3-}$ is similar to that of the Mo-Fe-cofactor of nitrogenase. Detailed magnetic and theoretical studies have been done and the complex has been formulated as an Fe(I) ($S = 3/2$) complex [104] coordinated to two $(\text{MoS}_4)^{2-}$ ligands. However, the isoelectronic cobalt complex $[\text{Co}(\text{MoS}_4)_2]^{2-}$ does not show any EPR signals even at temperatures as low as 10 °K. However the magnetic susceptibility data for the cobalt complexes are consistent with an $S = 3/2$ formalism [124].

1.10.4 Mossbauer spectroscopy

^{57}Fe Mössbauer spectra provide a direct means of investigating the electronic environment about the Fe atoms [74,75]. The ^{57}Fe Mössbauer spectra of the $\{\text{MoFe}_3\text{S}_4\}$ double cubane complexes exhibit an asymmetric quadrupole doublet suggesting that the Fe atoms are not strictly equivalent. Using known Fe-S complexes and Fe-S phases as standards the observed isomer shifts for the $\{\text{MoFe}_3\text{S}_4\}$ units in the double cubane clusters have been attributed to mean oxidation states of Fe of +2.5 to +2.67. The ^{57}Fe isomer shifts of the linear $[\text{Fe-M-S}]$ complexes are intermediate in magnitude to values reported for the tetrahedral Fe(II)S_4 and Fe(III)S_4 chromophores suggesting a formal oxidation state between +2 and +3 for the iron atoms and provide a direct evidence for the $\text{Fe} \rightarrow \text{M}$ charge transfer in these complexes. Complexes with more electronegative ligands on Fe like $[\text{Cl}_2\text{FeMoS}_4]^{2-}$ 7a [106], $[(\text{PhO})_2\text{Fe}(\text{MoS}_4)]^{2-}$ 7c [114], exhibit larger isomer shifts and quadrupole splittings indicating significantly greater Fe(II) character and therefore less electron donation from Fe to Mo. The

isomer shift values for the trinuclear complexes $[(\text{FeCl}_2)_2\text{MS}_4]^{2-}$ 10 [109] is indicative of a formal +2 oxidation state of the iron atoms. This apparent reduction in charge transfer in the trimers is not surprising since two iron atoms compete for charge transfer to the central Mo or W. The Mössbauer results also indicate that in $[\text{Fe-M-S}]$ complexes the electronic environment of iron atoms, to a first approximation is rather insensitive to a change from Mo to W.

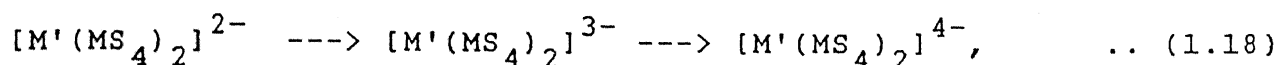
1.11. Magnetic Susceptibility Measurements:

Magnetic measurements have been mainly used to clarify the structures of the Ni and Co complexes. The bis(thiometallato) complexes of $[\text{M}'(\text{MS}_{4-n}\text{O}_n)_2]^{2-}$ ($\text{M}' = \text{Ni, Pd, Pt}$; $\text{M} = \text{Mo, W}$) are all diamagnetic and thus all these complexes are squareplanar [60-66]. The magnetic moments of the Co-thiometallato complexes are essentially closer to spin-only values of "typical" compounds with a tetrahedral CoS_4 chromophore because of the strong $\text{Co} \rightarrow \text{M}$ electron delocalization [124]. The linear $[\text{Fe-M-S}]$ clusters exhibit a variety of spin states [74,75]. The complex trianion $[\text{Fe}(\text{MoS}_4)_2]^{3-}$ obeys Curie-Weiss law with $C = 1.85 \pm 0.002$ and $\theta = -1.41 \pm 0.09$ °K in the temperature range 200-6 °K [104]. The room temperature magnetic moments of the dimeric complexes $[\text{X}_2\text{Fe}(\text{MoS}_4)]^{2-}$ [$\text{X} = \text{Cl}$ or RS^-] are very close to the spin-only value of 4.93 BM per formula unit, with a high-spin Fe(II)-Mo(VI) formulation. The dinitrosyl complexes $[(\text{NO})_2\text{FeMoS}_4]^{2-}$ are diamagnetic. The magnetic moments of the trinuclear complexes $[(\text{FeCl}_2)_2\text{MS}_4]^{2-}$ [109] complexes are lower than that expected for two, non-interacting, high-spin ($S = 2$) Fe(II) ions. Temperature

dependence studies of the magnetic susceptibilities of these complexes show weak antiferromagnetic behavior.

1.12 Electrochemistry

The ability of the tetrathiomallate ligands to stabilize relatively reduced oxidation states of the central metal ions M' in complexes such as $[M'(MS_4)_2]^{n-}$ is demonstrated by the existence of the three-membered electron transfer series,



where $M' = Co, Ni, Pd, Pt$; $M = Mo, W$ and by the isolation of the trianionic species of the type $[Fe(MS_4)_2]^{3-}$ and $[Co(MS_{4-n}O_n)_2]^{3-}$.

The bis(thiomallato) complexes of $Ni(II)$, show two isolated and sequential reversible one-electron reduction waves [66]. The bis(thiomallato) complexes of $Pd(II)$ exhibit two sequential reductions but at potentials much closer together than the analogous nickel complexes. The first reduction is reversible while the second reduction is irreversible. The analogous Pt complexes exhibit a single reduction wave. It has been reported, that the cyclic voltammograms of Pt -thiomallate complexes is indicative of an overlap of two reduction waves. All the bis-(thiomallato) complexes of Ni, Pd and Pt show irreversible, multielectron oxidations, probably localized on the terminal sulfur atoms of the thiomallates [66]. The electrochemical data of some thiomallato complexes are summarised in Table 1.6. The electrochemical data clearly indicate that the reduction potentials for the bis(thiomallato) complexes increase in the order $Fe < Co < Ni < Pd < Pt$. It is also evident that increasing the oxygen content of the thiomallate ligand results in an

Table 1.6

Electrochemical data of some thiometallato complexes

Complex	E(1)	E(2)	Ref
$[\text{Fe}(\text{MoS}_4)_2]^{2-}$	-070	-	102
$[\text{Fe}(\text{WS}_4)_2]^{2-}$	-270	-	103
$[\text{Co}(\text{MoS}_4)_2]^{2-}$	-360	-	124
$[\text{Co}(\text{WS}_4)_2]^{2-}$	-550	-	124
$[\text{Co}(\text{MoOS}_3)_2]^{2-}$	-450	-	124
$[\text{Co}(\text{WOS}_3)_2]^{2-}$	-620	-	124
$[\text{Co}(\text{MoO}_2\text{S}_2)_2]^{2-}$	-780	-	124
$[\text{Co}(\text{WO}_2\text{S}_2)_2]^{2-}$	-840	-	124
$[\text{Ni}(\text{MoS}_4)_2]^{2-}$	-606	-1396	66
$[\text{Ni}(\text{WS}_4)_2]^{2-}$	-614	-1573	66
$[\text{Pd}(\text{MoS}_4)_2]^{2-}$	-1073	-1270	66
$[\text{Pd}(\text{WS}_4)_2]^{2-}$	-1066	-1310	66
$[\text{Pt}(\text{MoS}_4)_2]^{2-}$	-1301	-	66
$[\text{Pt}(\text{WS}_4)_2]^{2-}$	-1346	-	66
$[(\text{bipy})_2\text{RuMoS}_4]$	-1500	-1750	130

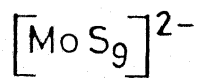
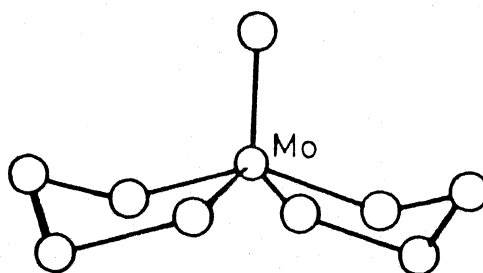
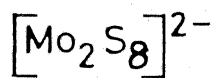
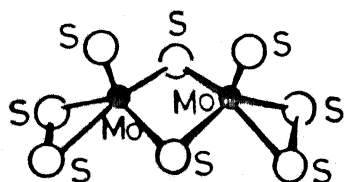
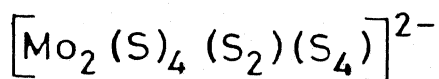
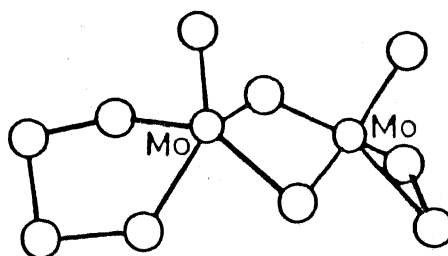
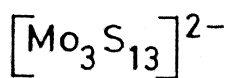
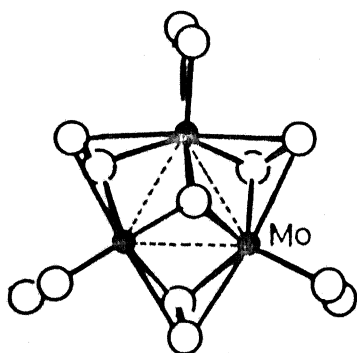
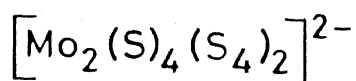
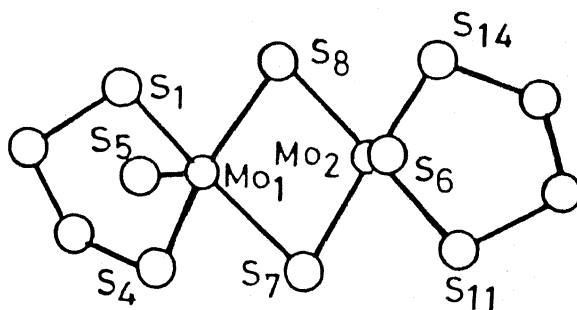
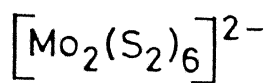
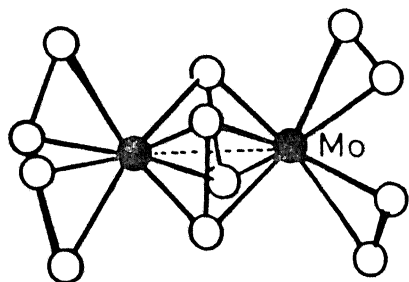
E values are in mV relative to SCE

increasing difficulty of reduction (Table 1.6). The complex $[(bipy)_2RuMoS_4]$ displays an irreversible anodic and two quasi-reversible cathodic waves in its cyclic voltammogram. The irreversible anodic wave has been attributed to the oxidation process of Ru(II) to Ru(III) and the cathodic waves have been assigned to the reduction of 2,2'-bipyridine [130].

1.13 X-ray diffraction studies:

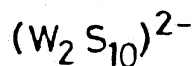
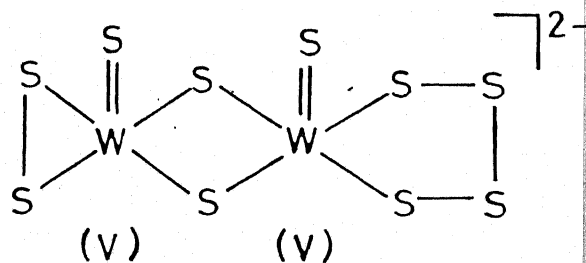
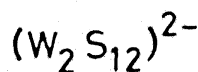
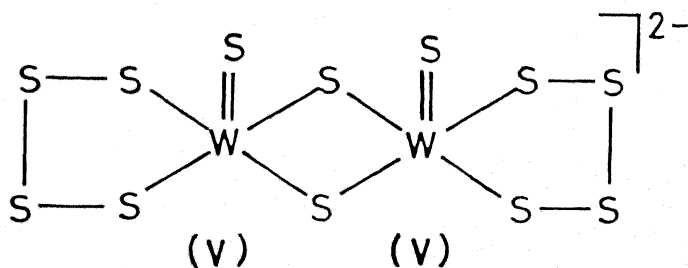
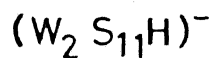
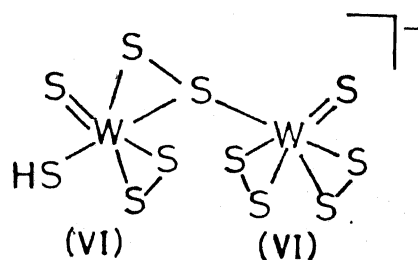
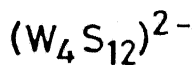
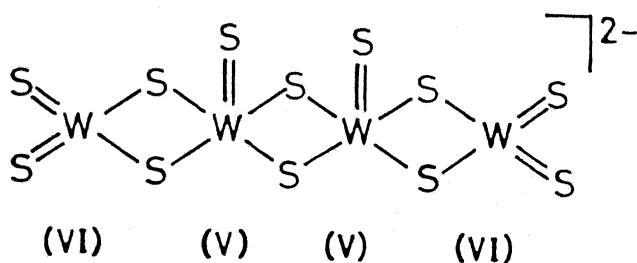
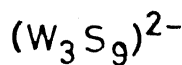
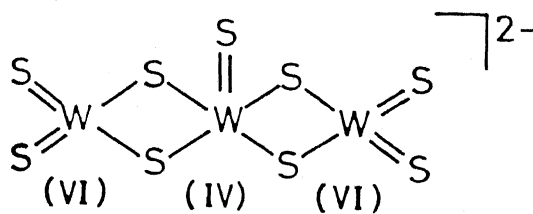
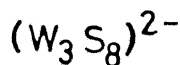
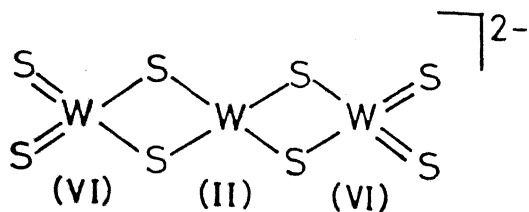
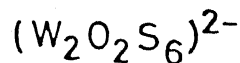
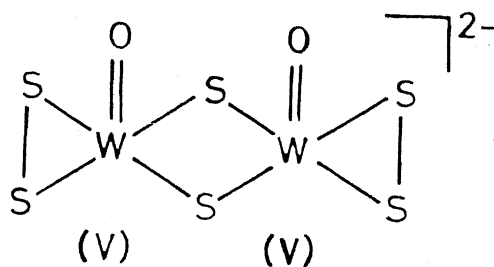
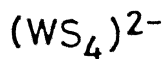
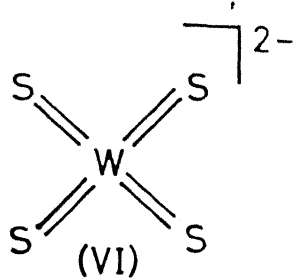
A single crystal examination of $(NH_4)_2MoS_4$ has shown it to be isomorphous with β - K_2SO_4 [21]. The alkali metal and ammonium salts of the thiometallates have been examined by X-ray powder diffraction and it has been shown that all are isostructural, barring the Tl salts and $(NH_4)_2Mo_2S_2$ [151-153]. The Mo-S bond length in $(NH_4)_2MoS_4$ is 2.19 Å which is intermediate between that of a Mo-S single bond and Mo=S double bond indicating the involvement of π -bonding.

The versatile ligational nature of the disulfide and polysulfide ligands are witnessed in the poly(thiometallates) described earlier [35,154]. Representative structures of some Mo/W-sulfido anions are depicted in Figs 1.9 & 1.10. The structures of the homometallic complexes $[M_3S_9]^{2-}$ (M=Mo, W) consists of two tetrahedral bidentate $[MoS_4]^{2-}$ units bound to a central square pyramidal $\{MS\}^{2+}$ unit [47]. Similarly the trimetallic complex $[W_3S_8]^{2-}$ consists of a central W^{2+} bound by two $[WS_4]^{2-}$ units one on each side [53]. The central W atom has a squareplanar coordination of S atoms, while the terminal W atoms have a tetrahedral coordination. In general the $M-S_{term}$ bond lengths are shorter than the $M-S_{br}$ bonds.



STRUCTURE TYPES OF SOME MOLYBDENUM-SULFIDO ANIONS.

FIG. 1.9



STRUCTURE TYPES OF TUNGSTEN-SULFIDO ANIONS

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The Mo-S bond length in the polymeric complex $\text{NH}_4\text{CuMoS}_4$ is 2.19 Å. The structure of this complex consists of a tetrahedral arrangement of S atoms around each Mo and Cu atoms, with each tetrahedron sharing two corners with two of its neighbours [124]. The thiomolybdate can be visualized as a doubly bridging ligand in this complex.

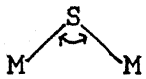
The structures of many thiometallato complexes have been solved by single crystal X-ray studies. The structures of representative types of $\{\text{M}'\text{-MS}_4\}$ (M' =heterometal; $\text{M}=\text{Mo}, \text{W}$) complexes are depicted in Figs 1.2 & 1.5 and selected structural parameters are listed in Table 1.7 [12,74,75]. A feature common to all of these complexes is the nearly planar $\{\text{M}'(\mu\text{-S})_2\text{M}\}$ dimetallic unit. The M-S_{br} and M-S_{term} distances in all the thiometallato complexes lie in the range 2.25 ± 0.01 Å and 2.16 ± 0.02 Å respectively while the M-S bond length in the free ligand $[\text{MoS}_4]^{2-}$ is 2.18 Å. The M-S bond distances suggest a formal oxidation state of +6 for $\text{M}=\text{Mo}, \text{W}$ in all these complexes.

In bis(thiometallato) complexes of the type $[\text{M}'(\text{MS}_4)_2]^{2-}$ the arrangement of the S atoms around the heterometal depends upon the nature of the central metal. When $\text{M}'=\text{Ni}, \text{Pd}, \text{Pt}$, the complexes are square-planar whereas the complexes with $\text{M}'=\text{Co}, \text{Zn}$ are tetrahedral. In all these complexes the M-S_{term} bond lengths are shorter than that of the M-S_{br} bond length. The $\text{M}'\dots\text{M}$ separation is of the order ~ 2.8 Å (Table 1.7) [67-69].

In the trinuclear complex $[(\text{FeCl}_2)_2\text{MoS}_4]^{2-}$ where the $[\text{MoS}_4]^{2-}$ bridges the two FeCl_2 units, all the sulfurs are bridging sulfurs and the Mo-S bond length is 2.204 Å.

Table 1.7

X-ray data of some thiometallato complexes

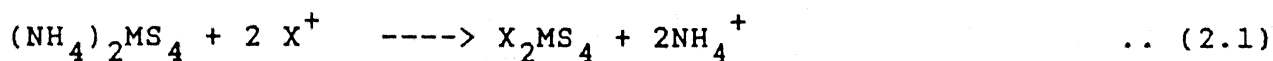
Complex	M-S _{br}	M-S _{term} Å	M---M'		Ref
(NH ₄) ₂ MoS ₄	-	2.178	-	-	21
(NH ₄)CuMoS ₄	2.19	-	2.70	-	126
[Cl ₂ FeMoS ₄] ²⁻	-	-	2.775	75.6	106
[(PhS) ₂ FeMoS ₄] ²⁻	2.246	2.154	2.750	75.5	112
[(S ₅)FeMoS ₄] ²⁻	2.253	2.145	2.731	74.3	113
[(S ₅)FeWS ₄] ²⁻	2.254	2.157	2.753	74.9	113
[(FeCl ₂) ₂ MoS ₄] ²⁻	2.204	-	2.775	76.1	109
[Fe(MoS ₄) ₂] ³⁻	2.256	2.171	2.740	74.8	101
[Fe(WS ₄) ₂ (DMF) ₂] ²⁻	2.213	2.164	3.044	80.0	70
[Co(WS ₄) ₂] ²⁻	2.219	2.139	2.798	77.4	68
[Ni(MoS ₄) ₂] ²⁻	2.227	2.151	2.798	77.9	67
[Ni(WS ₄) ₂] ²⁻	2.232	2.151	2.817	78.2	12
[Zn(WS ₄) ₂] ²⁻	2.233	2.156	2.927	78.5	69

The Mo-Fe distances observed for the linear [Fe-Mo-S] model complexes mentioned earlier are of the order $\sim 2.8 \text{ \AA}$ and these values are comparable to those found by EXFAS for the Mo site of nitrogenase [78]. However the Mo-S distances observed in the linear Fe-Mo-S clusters are substantially shorter than the 2.35 \AA found by EXFAS for the four S nearest neighbours of Mo in nitrogenase. From the X-ray studies of linear [Fe-Mo-S] clusters it has been inferred that the Mo site in the Fe-Mo-co is relatively reduced and more accurate linear cluster models will have to utilize Mo in oxidation state lower than +6 or +5 [74].

CHAPTER 2

SCOPE OF THE WORK

The synthetic aspects, reactivity and spectroscopic investigations of the thiometallates have been discussed in the preceding chapter. The thiometallates can be easily prepared as the water soluble alkali metal or ammonium salts in good yields. Cation exchange reactions of the thiometallates have been well studied. Thus for example the aqueous reactions of the ammonium thiometallates with bulky cations like Cs^+ , PPh_4^+ etc., result in the exchange of NH_4^+ for the bulky cation as follows:



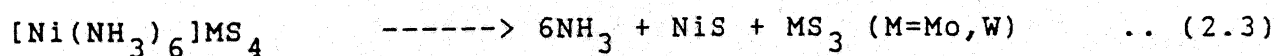
where $\text{M}=\text{Mo}, \text{W}$; $\text{X}=\text{Rb}, \text{Cs}, \text{PPh}_4, \text{AsPh}_4$

The attempted exchange of the ammonium ions for divalent metal cations like Fe, Co, Ni, Zn results in the formation of a mixture of X-ray amorphous sulfides as shown below [155].



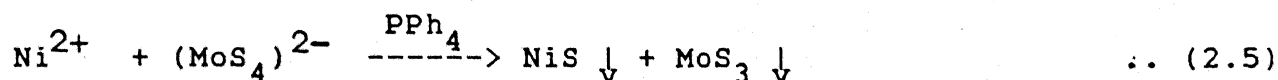
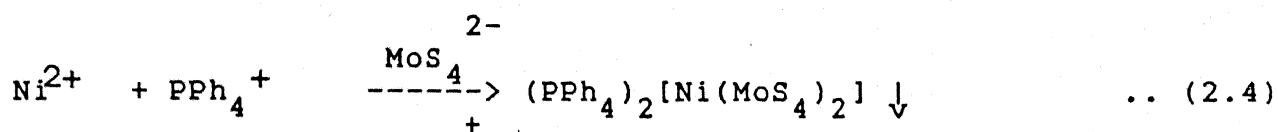
where $\text{M}'=\text{Fe}, \text{Co}, \text{Ni}, \text{Mn}$

In contrast, discrete salts like $[\text{M}'(\text{NH}_3)_6]\text{MS}_4$ ($\text{M}'=\text{Co}, \text{Ni}$) [156] have been isolated (Table 1.1). It is interesting to note that the aquated transition metal salts lead to the formation of amorphous sulfides whereas the use of hexamine complexes produce discrete salts. However the thiometallate salts of these complex cations $[\text{M}'(\text{NH}_3)_6]^{2+}$ are not very stable as they slowly decompose with the evolution of ammonia and form amorphous sulfides.



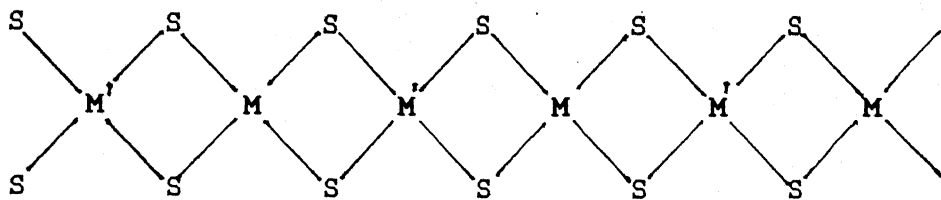
The reactions of cupric salts with tetrathiomolybdate results in the reduction of Cu(II) to Cu(I) and the formation of the polymeric species $\text{NH}_4\text{CuMoS}_4$ [126].

The aqueous reactions of thiometallates with bivalent metal ions in the presence of bulky cations like PPh_4^+ leads to the formation of bis(thiometallato) complexes of the type $[\text{M}'(\text{MS}_4)_2]^{2-}$ ($\text{M}' = \text{Fe}, \text{Co}, \text{Ni}, \text{Pd}, \text{Pt}, \text{Zn}, \text{Cd}, \text{Hg}$) [11, 12]. This has been discussed at length in the previous chapter. A very important point to be noted is that the bulky cation should already be present in the reaction medium prior to the mixing of the transition metal salt with thiometallate.



In a typical reaction an aqueous solution containing the transition metal salt and PPh_4^+ is mixed with an aqueous solution of the thiometallate. The mixing of M'^{2+} with MoS_4^{2-} results in the immediate formation of X-ray amorphous sulfides. So the clue to the formation of such discrete complex anions of the type $[\text{M}'(\text{MS}_4)_2]^{2-}$ lies in the use of bulky cations which can trap the complex anions. But in the reaction of Fe(II) with $(\text{MoS}_4)^{2-}$, even the use of $(\text{PPh}_4)^+$ does not afford any discrete complexes but only a polymeric species of approximate composition $[\text{Fe}(\text{MoS}_4)_2]^{2-}$.

From powder diffraction studies and resonance Raman spectroscopic investigations it has been concluded that catena units of the type shown below are present in the polymeric species [157].



The polymerization tendency and the sulfide formation in the aqueous reactions of thiometallates with transition metals can be effectively stopped by the use of coligands which can coordinate to the heterometal resulting in the formation of discrete mixed ligand bimetallic complexes. The usefulness of the coligands can be rationalized from the reaction of cupric salts with thiometallates. As stated earlier Cu^{2+} with $(\text{NH}_4)_2\text{MoS}_4$ gives the polymeric species $\text{NH}_4\text{CuMoS}_4$. Recently it has been demonstrated that the same reaction in the presence of aromatic diimines or triphenylphosphine can terminate polymerization and discrete compounds can be isolated [129].

In all the bis(thiometallato) complexes of Ni, Co, Pd, Pt, Zn, Cd, Hg, Fe discussed in the previous chapter the heterometal is always tetracoordinated by S atoms and the geometry around the central metal is either square planar or tetrahedral. In the case of iron, the coordination sphere around Fe has been modified and mixed ligand complexes like $(\text{Cl}_2\text{FeMS}_4)^{2-}$ ($\text{M}=\text{Mo}, \text{W}$) have been isolated. The synthesis of all such mixed ligand complexes and the trimetallic species $[\text{Fe}(\text{MoS}_4)_2]^{3-}$ have been achieved in non-aqueous medium [74, 75].

The aromatic diimines 2,2'-bipyridine and 1,10-phenanthroline are well known and frequently used as ligands in coordination chemistry. The metal complexes of these and related ligands have been well documented in the literature [158]. The tris(diimine) complexes of iron(II), $[\text{Fe}(\text{L-L})_3]^{2+}$ are interesting as they undergo ligand displacement reactions with monodentate and bidentate anionic ligands and a rich chemistry of such neutral complexes $[\text{Fe}(\text{L-L})_2\text{X}_2]$ is well established [159,160]. Thus the use of aromatic diimines in the reaction system $\text{Fe}^{2+}/(\text{MoS}_4)^{2-}/\text{H}_2\text{O}$ provides a tailor-made Fe source which can undergo both ligand displacement reactions and afford stable coligands on the Fe site preventing polymerization. The use of these neutral ligands also excludes the use of bulky cations. Depending upon the reaction conditions one can expect the formation of salt-like species which may further rearrange to form sulfur bridged heterometallic complexes. In this methodology the possibility of ending up in hexacoordinated as well as tetracoordinated Fe species exists. If a simple ligand displacement reaction occurs as expected, then the heterometal complexes will be of 1:1 stoichiometry. Under extreme conditions, the coordination of all the four S atoms in the thiometallate resulting in the formation of a trinuclear cationic complex with the thiometallate bridged between the two iron centres can be achieved.

The reactions in the system $\text{Fe}^{2+}/\text{MoS}_4^{2-}/\text{H}_2\text{O}$ which is of bio-inorganic interest are complicated. The epr studies of the Fe-Mo protein of the enzyme nitrogenase have shown it to exhibit an epr signal with apparent g values at 4.32, 3.65 and 2.01 due to an

S = 3/2 spin system [161]. This signal vanishes when 1,10-phenanthroline is added but prevails in the presence of 2,2'-bipyridine [162,163]. Thus the interactions of these aromatic diimines in the system $\text{Fe}^{2+}/\text{MoS}_4^{2-}/\text{H}_2\text{O}$ assume bioinorganic importance.

It goes without saying that the solvent plays a vital role in the formation of complexes and the solvent effect is an important factor to be considered in synthetic chemistry. Thus for example, the polymeric species $[\text{Fe}(\text{MoS}_4)_2]$ has been isolated from aqueous reactions of Fe(II) salts with tetrathiomolybdate and discrete species $[\text{Fe}(\text{MoS}_4)_2]^{3-}$ from the reaction of Fe(II) xanthate with MoS_4^{2-} in CH_2Cl_2 [65,101]. Hence the study of the ligational behavior of thiometallates with transition metals in the presence of aromatic diimines in non-aqueous solvents can be carried out to understand the role played by solvent in the synthesis of mixed ligand complexes. Another aspect of this study is to see the trend in the reactivity between tetrathiometallates and oxotrithiometallates which is important from the coordination chemistry point of view. If the proposed scheme of action is going to result in the formation discrete heterometal complexes then more ambitious attempts to synthesize heterometal aggregates with other transition metals can be attempted.

Manganese complexes with S donor ligands, like the tetrahedral $[\text{Mn}(\text{S}_6)(\text{S}_5)]^{2-}$ [164] and the octahedral $[\text{Mn}(\text{Et}_2\text{dtc})_3]$ (dtc=dithiocarbamate) [165] are known but the attempted synthesis of the sulfur ligated Mn-thiometallate complex by many workers has not been successful. A recent attempt by Manoli and

coworkers to synthesize the bis(thiometallato) complex $[\text{Mn}(\text{WS}_4)_2]^{2-}$, analogous to the well established bis(thiometallato) complexes of Ni, Pd, Pt, Zn, . Cd, Hg, Co has resulted in the formation of a binary W-S compound $[\text{W}_2\text{S}_{11}]^{2-}$ without any incorporation of Mn [57]. Thus the use of aromatic diimines in the synthesis of Mn-thiometallate complexes is worth trying.

The compounds isolated using the above mentioned synthetic strategies can be subjected to physico-chemical studies to gather useful information on the structure and the nature of bonding.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 GENERAL CONSIDERATIONS:

All the reactions were carried out in air, unless specified otherwise. Distilled water and singly distilled ethanol were used in the preparation of the complexes. The metal salts, 2,2'-bipyridine and 1,10-phenanthroline monohydrate were of analytical grade and were used as purchased.

3.1.1 Methods of analysis and work-up manipulations

The elements carbon, hydrogen and nitrogen were analyzed by standard microanalytical techniques at the Indian Institute of Technology, Kanpur. The procedures employed for the analysis of other elements are as follows:

Sulfur

About 150 mg of the sulfur containing compound was oxidized with an excess of alkaline bromine water. The excess bromine was evaporated off by warming the solution slowly. To the resulting solution, hydrochloric acid was added slowly and the liberated bromine was again evaporated off. The solution was filtered and the sulfate in the filtrate was estimated gravimetrically as barium sulfate by the standard method [166].

Cobalt and Nickel

An amount of the cobalt or nickel containing compound (200 mg) was decomposed by treating with an excess of aqua regia. The resulting solution was evaporated to dryness and the aqua

regia treatment was repeated again to ensure complete decomposition of the compound. The residue was redissolved in concentrated hydrochloric acid and the solution was evaporated to dryness. The residue was washed several times with warm water and the washings containing the cobalt/nickel chloride were collected after filtering. The nickel in the filtrate was estimated gravimetrically as the dimethylglyoximate by the standard method. For compounds containing cobalt, the cobalt in the filtrate was estimated as the tetrapyridinebis(thiocyanato)-cobalt(II) by using the standard procedure [166] .

3.2 SYNTHESSES OF THIOMOLYBDATES AND THIOTUNGSTATES: [13,14]

3.2.1 Preparation of ammonium tetrathiomolybdate

Ammonium heptamolybdate (5.0 g) was dissolved in a mixture of conc. ammonium hydroxide (30 mL) and water (10 mL) and the solution filtered . Hydrogen sulfide gas was passed rapidly into the filtrate. The color of the solution initially was yellow and gradually changed to red. After passing hydrogen sulfide gas for 30 min, red crystals started depositing. The passing of the gas was stopped and the deep red solution was cooled at 0 °C for 20 min. The red crystals of ammonium tetrathiomolybdate were isolated by filtration, washed with a little cold water, ethanol and ether and dried in vacuo. Yield 80% .

The compound gave a characteristic band at 480 cm^{-1} in the IR spectrum due to ν_{as} (MoS) vibration.

3.2.2 Preparation of ammonium tetrathiotungstate

Sodium tungstate (5.0 g) was dissolved in a mixture of conc. ammonium hydroxide (40 mL) and water (10 mL). The solution was warmed to 60 °C and hydrogen sulfide gas was bubbled into it for 9 h by maintaining the temperature at 60 °C. The solution was cooled at 10 °C to yield the orange-yellow ammonium tetrathio-tungstate. The product was filtered, washed with a little amount of cold water, ethanol and ether and dried in vacuo. Yield 50% .

The IR spectrum of the compound showed a characteristic band at 460 cm^{-1} due to ν_{as} (WS) vibration.

3.2.3 Preparation of cesium oxotriithiomolybdate

Ammonium heptamolybdate (5.0 g) and cesium chloride (15.0 g) were dissolved in a mixture of water (20 mL) and conc. ammonium hydroxide (15 mL). Conc. acetic acid (8 mL) was added to this solution and hydrogen sulfide gas was bubbled into it for 15 min at room temperature. The gas passing was stopped as soon as orange-red crystals started appearing. The solution was cooled in an ice-bath for 5 min and the orange-red crystals were isolated by filtration. The crystals were washed with a little amount of cold water, followed by ethanol and finally with ether and dried under vacuum. Yield 78% .

The IR spectrum of the compound showed characteristic bands at 862 cm^{-1} and 480 cm^{-1} due to ν_{as} (MoO) and ν_{as} (MoS) vibrations, respectively.

3.2.4 Preparation of ammonium oxotritthiotungstate

Sodium tungstate (5.0 g) was dissolved in a mixture of water (5 mL) and conc. ammonium hydroxide (20 mL) and the solution filtered. Hydrogen sulfide gas was bubbled rapidly into the filtrate for 25 min at room temperature. A small amount of ammonium dioxodithiotungstate separated out. The reaction mixture was filtered rapidly into ice cold iso-propanol (500 mL) and the product separated out as a yellow powder. The yellow powder was isolated by filtration washed well with iso-propanol and ether and dried under vacuum. Yield 74% .

The IR spectrum of the compound gave bands at 860 cm^{-1} and 470 cm^{-1} due to $\nu_{\text{as}}(\text{WO})$ and $\nu_{\text{as}}(\text{WS})$ vibrations, respectively.

3.3 SYNTHESSES OF Mn-THIOMETALLATE COMPLEXES:

3.3.1 Preparation of $[(\text{bipy})_2\text{MnS}_2\text{MoS}_2]$

Ammonium tetrathiomolybdate (260 mg, 1 mmol) was dissolved in water (20 mL) and a drop of ammonium hydroxide was added to this, and the solution filtered. A solution containing manganous chloride tetrahydrate (200 mg, 1 mmol) in water (5 mL) and 2,2'-bipyridine (320 mg, 2 mmol) in ethanol (15 mL) was added slowly in drops with stirring to the clear tetrathiomolybdate solution. The color of the solution changed immediately and after a few min. a dark brown solid separated out. The stirring was continued for 2 h and then the product was isolated by filtration. The product was washed several times with water, followed by ethanol and ether and dried in vacuo. Yield 90% .

Anal. Found (Calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_4\text{MnMoS}_4$): C, 40.95 (40.61); H, 3.02 (2.71); N, 9.68 (9.48); S, 21.68 (21.66).

3.3.2 Preparation of $[(o\text{-phen})_2\text{MnS}_2\text{MoS}_2]$

The procedure employed for the preparation and isolation of this complex was similar to the one given above for its bipyridine analog except that 1,10-phenanthroline monohydrate (400 mg) was used in place of 2,2'-bipyridine. The brown product that was obtained, was washed with water, ethanol, ether and dried under vacuum. Yield 80%.

Anal. Found (Calcd. for $\text{C}_{24}\text{H}_{16}\text{N}_4\text{MnMoS}_4$): C, 45.25 (45.07); H, 2.32 (2.50); N, 8.62 (8.76); S, 20.2 (20.03).

3.3.3 Preparation of $[(\text{bipy})_2\text{MnS}_2\text{WS}_2]$

Manganous chloride tetrahydrate (200 mg, 1 mmol) and 2,2'-bipyridine (320 mg, 2 mmol) were dissolved in a mixture of water (5 mL) and ethanol (20 mL) and this solution was slowly added in drops to a well stirred solution of ammonium tetrathiotungstate (350 mg, 1 mmol) in water (25 mL). An orange-yellow solid slowly separated out. The stirring was continued for 3 h and the solid isolated by filtration. The product was washed several times with water, followed by ethanol and finally with ether and dried in a vacuum dessicator. The yield was quantitative.

Anal. Found (Calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_4\text{MnWS}_4$): C, 35.72 (35.35); H, 2.48 (2.36); N, 8.45 (8.25); S, 19.02 (18.85).

3.3.4 Preparation of $[(o\text{-phen})_2\text{MnS}_2\text{WS}_2]$

The procedure employed for the preparation and isolation of this complex is identical to the one used for its bipyridine analog except that 1,10-phenanthroline monohydrate (400 mg) was used in place of 2,2'-bipyridine. The orange-yellow solid

thus obtained was washed well with water, ethanol and ether and dried in a vacuum dessicator. Yield 80%

Anal. Found (Calcd. for $C_{24}H_{16}N_4MnWS_4$): C, 40.02 (39.61); H, 2.50 (2.20); N, 8.05 (7.70); S, 17.43 (17.61).

3.3.5 Preparation of $[(bipy)_2MnS_2MoOS]$

Cesium oxotriithiomolybdate (475 mg, 1 mmol) was dissolved in water (50 mL) and the solution filtered. A solution containing manganous chloride tetrahydrate (200 mg, 1 mmol) in water (5 mL) and 2,2'-bipyridine (320 mg, 2 mmol) in alcohol (20 mL) was prepared. This solution was added dropwise with stirring to the oxotriithiomolybdate solution. A light brown colored solid separated out. The stirring was continued for an hour and the reaction mixture was filtered to isolate the light brown solid. The product was washed thoroughly with water, ethanol and ether and dried under vacuum. Yield 85%.

Anal. Found (Calcd. for $C_{20}H_{16}N_4MnMoOS_3$): C, 41.95 (41.74); H, 3.02 (2.78); N, 9.85 (9.74); S, 16.75 (16.70).

3.3.6 Preparation of $[(o-phen)_2MnS_2MoOS]$

The compound was prepared by employing the same procedure used for its bipyridine analog. 1,10-Phenanthroline (400 mg) was used in place of 2,2'-bipyridine to yield the light brown product. The product was washed with water, ethanol, and ether and dried under vacuum. Yield 80% .

Anal. Found (Calcd. for $C_{24}H_{16}N_4MnMoOS_3$): C, 46.85 (46.23); H, 2.95 (2.57); N, 9.55 (8.99); S, 15.22 (15.41).

3.3.7 Preparation of $[(bipy)_2MnS_2WOS]$

Manganous chloride tetrahydrate (100 mg, 0.5 mmol) and 2,2'-bipyridine (160 mg, 1 mmol) were dissolved in a mixture of water (5 mL) and ethanol (20 mL) and this solution was added dropwise, with stirring to a solution of ammonium oxotri-thiotungstate (165 mg, 0.5 mmol) in water (25 mL). A yellow solid precipitated slowly. The stirring was continued for 4 h and the solution filtered. The product was washed several times with water, ethanol, and ether and dried in a vacuum dessicator. Yield 65%.

Anal. Found (Calcd. for $C_{20}H_{16}N_4MnWOS_3$): C, 36.56 (36.20); H, 2.62 (2.41); N, 8.17 (8.45); S, 14.85 (14.48).

3.3.8 Preparation of $[(o-phen)_2MnS_2WOS]$:

The preparation of this complex was similar to that of the corresponding bipyridine analog. 1,10-Phenanthroline monohydrate (200 mg, 1 mmol) was used in place of 2,2'-bipyridine and the yellow complex thus obtained was washed with copious amounts of water, ethanol and ether and dried under vacuum. Yield 60%

Anal. Found (Calcd. for $C_{24}H_{16}N_4MnWOS_3$): C, 40.39 (40.51); H, 2.75 (2.25); N, 8.21 (7.88); S, 13.12 (13.5).

3.4 SYNTHESSES OF Fe-THIOMETALLATE COMPLEXES:

3.4.1 Preparation of $[(bipy)_2FeS_2MoS_2]$

Method A: A solution of tris(bipyridine)iron(II) sulfate, prepared by dissolving Mohr's salt (400 mg, 1 mmol) and 2,2'-bipyridine (480 mg, 3 mmol) in a mixture of water (40 mL) and ethanol (10 mL), was slowly added in drops to a well stirred

solution of ammonium tetrathiomolybdate (260 mg, 1 mmol) in water (20 mL) containing a drop of ammonium hydroxide. There was an immediate precipitation of a red microcrystalline compound. The stirring was continued for 8 h and then the solution was filtered. The product was washed several times with water, followed by ethanol and finally with ether and dried in a vacuum dessicator. Yield 65% .

Anal. Found (Calcd. for $C_{20}H_{16}N_4FeMoS_4$): C, 40.83 (40.54); H, 2.45 (2.70); N, 9.71 (9.46); S, 21.34 (21.62).

Method B: Ferrous chloride (125 mg, 1 mmol) was slowly added to a DMF solution (10 mL) of ammonium tetrathiomolybdate (260 mg, 1 mmol). The color of the solution changed to deep red. 2,2'-bipyridine (400 mg, 2.5 mmol) dissolved in DMF (10 mL) was slowly added into the deep red solution and the reaction mixture was warmed to 50 °C for 5 min. The solution was filtered and the filtrate was chilled overnight in a refrigerator to yield needle shaped crystals in 70% yield. The crystals were washed with a little water, ethanol and ether and dried in a vacuum dessicator. The red crystals thus obtained, gave an x-ray powder pattern identical to that of the compound obtained from method A and gave a satisfactory elemental analysis.

3.4.2 Preparation of $[(bipy)_2FeS_2WS_2]$

Method A: Ammonium tetrathiotungstate (350 mg, 1 mmol) was dissolved in water (25 mL) containing a drop of ammonia. The solution was kept under stirring and a solution containing tris(bipyridine)iron(II) sulfate, prepared by dissolving Mohr's salt (400 mg, 1 mmol) and 2,2'-bipyridine (480 mg, 3 mmol) in a

mixture of water (40 mL) and ethanol (10 mL) was slowly added to it. A red microcrystalline solid slowly separated out. The stirring was continued for 10 h. The solution was filtered to obtain the red crystals which were washed well with water, alcohol and ether and dried in vacuo. Yield 60% .

Anal. Found (Calcd. for $C_{20}H_{16}N_4FeWS_4$): C, 34.95 (35.29); H, 2.44 (2.35); N, 8.15 (8.24); S, 19.01 (18.82).

Method B: Ferrous chloride (125 mg, 1 mmol) was slowly added to a DMF solution (10 mL) of ammonium tetrathiotungstate (350 mg, 1 mmol). The color of the solution changed to red. 2,2'-bipyridine (400 mg, 2.5 mmol) dissolved in DMF (10 mL) was slowly added into the red solution and the reaction mixture was warmed to 60 °C for 5 min. The solution was filtered and then left in the refrigerator. After 10 h fine red crystals separated out. The red crystals were isolated by filtration, washed with a little cold water, ethanol and ether and dried under vacuum. Yield 50% . The X-ray powder pattern of the compound thus obtained was identical with that of the compound obtained from the method A. The compound gave a satisfactory elemental analysis.

3.4.3 Preparation of $[(bipy)_2FeS_2MoOS]$

A solution of tris(bipyridine)iron(II) sulfate, prepared by dissolving Mohr's salt (400 mg, 1 mmol) and 2,2'-bipyridine (480 mg, 3 mmol) in a mixture of water (40 mL) and ethanol (10 mL), was slowly added in drops to a well stirred solution of cesium oxotrichiomolybdate (475 mg, 1 mmol) in water (80 mL). The color

of the oxotriithiomolybdate solution deepened and a red microcrystalline product was thrown out immediately. The stirring was continued for 6 h and the solution filtered. The product was washed thoroughly with water, followed by ethanol, ether and dried under vacuum. Yield 80% .

Anal. Found (Calcd. for $C_{20}H_{16}N_4FeMoOS_3$): C, 41.85 (41.67); H, 2.92 (2.78); N, 9.93 (9.72); S, 16.51 (16.67).

3.4.4 Preparation of $[(bipy)_2FeS_2WOS]$

A solution of tris(bipyridine)iron(II) sulfate prepared by dissolving Mohr's Salt (400 mg, 1 mmol) and 2,2'-bipyridine (480 mg, 3 mmol) in a mixture of water (40 mL) and ethanol (10 mL), was slowly added dropwise to a solution of ammonium oxotriithiotungstate (330 mg, 1 mmol) in water (20 mL) with stirring. The yellow color of the oxotriithiotungstate changed immediately to dark red and a red microcrystalline solid separated out of the solution. The stirring of the reaction mixture was continued for 8 h and the solution was filtered to isolate the product which was washed several times with water, ethanol and ether and dried under vacuum. Yield 70% .

Anal. Found (Calcd. for $C_{20}H_{16}N_4FeWOS_3$): C, 36.36 (36.14); H, 2.59 (2.41); N, 8.72 (8.43); S, 14.77 (14.46).

3.4.5 Preparation of $[(o-phen)_3FeMoS_4]$

Mohr's Salt (400 mg, 1 mmol) and 1,10-phenanthroline monohydrate (600 mg, 3 mmol) were dissolved in a mixture of water (40 mL) and ethanol (5mL), to give the red orange tris-(phenanthroline)iron(II) sulfate. This solution was slowly added

into an aqueous solution of ammonium tetrathiomolybdate, obtained by dissolving ammonium tetrathiomolybdate (260 mg, 1 mmol) in water (20 mL). A red solid separated out immediately. The solution was stirred for 8 h and the product was isolated by filtration. The compound was washed with water, ethanol and ether and dried in vacuo. The yield was quantitative.

Anal. Found (Calcd. for $C_{36}H_{24}N_6FeMoS_4$): C, 52.03 (52.68); H, 2.82 (2.93); N, 10.05 (10.24).

3.5 SYNTHESSES OF Co-THIOMETALLATE COMPLEXES :

3.5.1 Preparation of $[(bipy)_2CoS_2MoS_2]$

An aqueous solution (20 mL) of ammonium tetrathiomolybdate (260 mg, 1 mmol) was prepared. A solution of tris(bipyridine)-cobalt(II) chloride was prepared from cobaltous chloride hexahydrate (240 mg, 1 mmol) and 2,2'-bipyridine (480 mg, 3 mmol) in a mixture of water (5 mL) and ethanol (20 mL) was added slowly to the thiomolybdate solution with stirring. A red orange solid precipitated immediately. The stirring was continued for 3 h and the solution filtered. The product was washed well with water, ethanol and ether and dried under vacuum. Yield 79% .

Anal. Found (Calcd. for $C_{20}H_{16}N_4CoMoS_4$): C, 40.78 (40.34); H, 2.84(2.69); N, 9.52(9.41); S, 21.78(21.51); Co, 10.03 (9.92).

3.5.2 Preparation of $[(bipy)_2CoS_2WS_2]$

The procedure employed for the synthesis of this complex was similar to the one used for its molybdenum analog. Ammonium tetrathiotungstate (350 mg, 1 mmol) was used in place of ammonium tetrathiomolybdate. The yellow precipitate thus

obtained was washed well with water, ethanol and ether and dried under vacuum. Yield 80% .

Anal. Found (Calcd. for $C_{20}H_{16}N_4CoWS_4$): C, 35.37 (35.14); H, 2.52 (2.34); N, 8.41 (8.2); S, 19.01 (18.74); Co, 8.76 (8.64).

3.5.3 Preparation of $[(bipy)_2CoS_2MoOS]$

A solution of tris(bipyridine)cobalt(II) chloride was prepared from cobaltous chloride hexahydrate (240 mg, 1 mmol) and 2,2'-bipyridine (480 mg, 3 mmol) in a mixture of water (5 mL) and ethanol (25 mL). This was added in drops to an aqueous solution (60 mL) of cesium oxotrithiomolybdate (474 mg, 1 mmol) with stirring. An orange solid precipitated out immediately. The stirring was continued for 2 h and the solution was filtered. The orange precipitate was washed well with water, ethanol and ether and dried in vacuo. Yield 82% .

Anal. Found (Calcd. for $C_{20}H_{16}N_4CoMoOS_3$): C, 41.52 (41.45); H, 2.67 (2.76); N, 9.58 (9.67); S, 16.83 (16.58); Co, 10.37 (10.19).

3.5.4 Preparation of $[(bipy)_2CoS_2WOS]$

The compound was prepared by following the same procedure employed for its molybdenum analog. Ammonium oxotrithiotungstate (330 mg, 1 mmol) in water (20 mL) was used in place of cesium oxotrithiomolybdate to give an yellow precipitate. The precipitate was washed well with water, ethanol and ether and dried under vacuum. Yield 70% .

Anal. Found (Calcd. for $C_{20}H_{16}N_4CoWOS_3$): C, 36.21 (35.98); H, 2.51 (2.4); N, 8.52 (8.4); S, 14.68 (14.39); Co, 8.98 (8.85).

3.6 SYNTHESSES OF Ni-THIOMETALLATE COMPLEXES:

3.6.1 Preparation of $[(bipy)_2NiS_2MoS_2]$

An aqueous solution (25 mL) of ammonium tetrathiomolybdate (260 mg, 1 mmol) was prepared. After adding a drop of ammonia, the solution was filtered. An alcoholic solution (25 mL) of tris(bipyridine)nickel(II) chloride was prepared from nickel(II) chloride hexahydrate (240 mg, 1 mmol) and 2,2'-bipyridine (480 mg, 3 mmol) and this was added dropwise to a solution of ammonium tetrathiomolybdate with stirring. An orange-red solid precipitated immediately. The solution was stirred for 4 h and filtered. The precipitate was washed thoroughly with water, ethanol and ether and dried under vacuum. The yield was quantitative.

Anal. Found (Calcd. for $C_{20}H_{16}N_4NiMoS_4$): C, 40.58 (40.36); H, 2.81 (2.69); N, 9.73 (9.42); S, 21.76 (21.52); Ni, 9.95 (9.87);

3.6.2 Preparation of $[(o-phen)_2NiS_2MoS_2]$

This compound was prepared by following the same procedure used for its bipyridine analog. 1,10-phenanthroline monohydrate (600 mg, 3 mmol) was used instead of 2,2'-bipyridine. The compound was washed well with water, ethanol, ether and dried under vacuum. Yield 88% .

Anal. Found (Calcd. for $C_{24}H_{16}N_4NiMoS_4$): C, 45.15 (44.81); H, 2.63 (2.49); N, 8.89 (8.71); S, 19.98 (19.91); Ni, 9.40 (9.13).

3.6.3 Preparation of $[(bipy)_2NiS_2WS_2]$

An alcoholic solution (25 mL) of tris(bipyridine)nickel(II) chloride was prepared from nickel(II) chloride (240 mg, 1 mmol)

and 2,2'-bipyridine (480 mg, 3 mmol). The solution was slowly added in drops to a solution of ammonium tetrathiotungstate (350 mg, 1 mmol) in water (25 mL) with stirring. A yellow solid separated out immediately. The stirring was continued for 6 h and the solution filtered. The yellow product was washed well with water, ethanol and ether and dried in vacuo. The yield was quantitative.

Anal. Found (Calcd. for $C_{20}H_{16}N_4NiWS_4$): C, 35.38 (35.15); H, 2.82 (2.34); N, 8.45 (8.20); S, 18.92 (18.75); Ni, 8.75 (8.60).

3.6.4 Preparation of $[(o\text{-phen})_2NiS_2WS_2]$

The compound was prepared by following the same procedure used for its bipyridine analog. 1,10-phenanthroline monohydrate (600 mg, 3 mmol) was used instead of 2,2'-bipyridine. The compound was washed well with water, ethanol and ether and dried under vacuum. Yield 88%.

Anal. Found (Calcd. for $C_{24}H_{16}N_4NiWS_4$): C, 39.72 (39.41); H, 2.44 (2.19); N, 7.32 (7.66); S, 17.23 (17.52); Ni, 7.85 (8.03).

3.6.5 Preparation of $[(bipy)_2NiS_2MoOS_3]$

An aqueous solution (80 mL) of cesium oxotrichiomolybdate (480 mg, 1 mmol) was prepared. After adding a drop of ammonia, the solution was filtered. An alcoholic solution (25 mL) of tris(bipyridine)nickel(II) chloride was prepared from $NiCl_2 \cdot 6H_2O$ (240 mg, 1 mmol) and 2,2'-bipyridine (480 mg, 3 mmol) and this was added dropwise to a solution of ammonium tetrathiomolybdate with stirring. An orange-red solid precipitated immediately. The solution was stirred for 4 h and filtered. The precipitate was

washed thoroughly with water, ethanol and ether and dried under vacuum. The yield was quantitative.

Anal. Found (Calcd. for $C_{20}H_{16}N_4NiMoOS_3$): C, 41.73 (41.47); H, 2.92 (2.76); N, 9.85 (9.68); S, 16.84 (16.59); Ni, 10.35 (10.14).

3.6.6 Preparation of $[(o\text{-phen})_2NiS_2MoOS_3]$

This compound was prepared by following the same procedure used for its bipyridine analog. 1,10-phenanthroline monohydrate (600 mg, 3 mmol) was used instead of 2,2'-bipyridine. The compound was washed with water, ethanol, ether and dried under vacuum. Yield 88% .

Anal. Found (Calcd. for $C_{24}H_{16}N_4NiMoOS_3$): C, 46.23 (45.96); H, 2.71 (2.55); N, 8.77 (8.94); S, 15.56 (15.32); Ni, 9.56 (9.37).

3.6.7 Preparation of $[(bipy)_2NiS_2WOS_3]$

An alcoholic solution (25 mL) of tris(bipyridine)nickel(II) chloride was prepared from $NiCl_2 \cdot 6H_2O$ (240 mg, 1 mmol) and 2,2'-bipyridine (480 mg, 3 mmol) and this was added dropwise to a solution of ammonium oxotriethio-tungstate with stirring. A yellow solid precipitated immediately. The solution was stirred for 4 h and filtered. The precipitate was washed thoroughly with water, ethanol and ether and dried under vacuum. Yield 85% .

Anal. Found (Calcd. for $C_{20}H_{16}N_4NiWOS_3$): C, 36.12 (36.00); H, 2.55 (2.40); N, 8.48 (8.4); S, 14.19 (14.4); Ni, 8.62 (8.8).

3.6.8 Preparation of $[(o\text{-phen})_2NiS_2WOS_3]$

This compound was prepared by following the same procedure used for its bipyridine analog. 1,10-phenanthroline monohydrate (600 mg, 3 mmol) was used instead of 2,2'-bipyridine. The

compound was washed with water, ethanol and ether and dried under vacuum. Yield 88% .

Anal. Found (Calcd. for $C_{24}H_{16}N_4NiWOS_3$): C, 40.44 (40.30); H, 2.52 (2.24); N, 7.62 (7.84); S, 13.21 (13.43); Ni, 8.05 (8.21).

3.7 SYNTHESSES of TETRACOORDINATE Ni-THIOMETALLATE COMPLEXES:

3.7.1 Preparation of $[(bipy)NiS_2MoS_2]$

Method A: $NiCl_2 \cdot 6H_2O$ (240 mg, 1 mmol) and 2,2'-bipyridine (320 mg, 2 mmol) were dissolved in DMF (20 mL). The solution was warmed and added to a DMF solution (15 mL) containing ammonium tetrathiomolybdate (260 mg, 1 mmol). After allowing it to remain for 30 min, the solution was filtered off to remove NH_4Cl . Ethanol (25 mL) was added drop-wise to the filtrate and the solution was kept at $0^\circ C$ for 1 h to give dark brown crystals. The crystals were isolated by filtration and washed with a little amount of cold water, ethanol and ether and dried under vacuum. Yield 70%.

Anal. Found (Calcd. for $C_{10}H_8N_2NiMoS_4$): C, 27.57 (27.35); H, 2.02 (1.82); N, 6.56 (6.38); Ni, 13.12 (13.38); S, 29.04 (29.18).

Method B: An ethanolic solution (25 mL) of dichloro(bis)bipyridine nickel(II) was prepared from $NiCl_2 \cdot 6H_2O$ (240 mg, 1 mmol) and 2,2'-bipyridine (320 mg, 2 mmol). The lilac blue solution was added in drops to a solution of ammonium tetrathiomolybdate (260 mg, 1 mmol) in water (20 mL) with stirring. A brown precipitate separated out immediately and the reaction mixture was further stirred for 1 h and filtered. The brown product was isolated by filtration, washed well with

water, ethanol and ether and dried under vacuum. Yield 90% .
The compound gave satisfactory analysis.

3.7.2 Preparation of [(o-phen)NiS₂MoS₂]

NiCl₂.6H₂O (240 mg, 1 mmol) and 1,10-phenanthroline monohydrate (400 mg, 2 mmol) were dissolved in ethanol (25 mL) to give the lilac blue bis(phen)Ni(II) complex. The lilac blue solution was added in drops to a solution of ammonium tetrathiomolybdate (260 mg, 1 mmol) in water (20 mL) with stirring. A brown precipitate separated out immediately and the reaction mixture was further stirred for 1 h and filtered . The brown product was washed well with water, ethanol, ether and dried under vacuum. Yield 90% .

Anal. Found (Calcd. for C₁₂H₈N₂NiMoS₄): C, 31.32 (31.12); H, 1.85 (1.73); N, 6.23 (6.05); Ni, 12.52 (12.69); S, 27.51 (27.66).

3.7.3 Preparation of [(bipy)NiS₂WS₂]

Method A: A DMF solution (20 mL) of NiCl₂.6H₂O (240 mg, 1 mmol) and 2,2'-bipyridine (320 mg, 2 mmol) was prepared. The solution was warmed and added to a DMF solution (15 mL) containing ammonium tetrathiotungstate (350 mg, 1 mmol). After allowing it to remain for 30 min, the solution was filtered to remove NH₄Cl. Ethanol (25 mL) was added drop-wise to the filtrate and the solution was kept at 0 °C for 1 h to give dark brown crystals. The crystals were isolated by filtration and washed with a little amount of cold water, ethanol and ether and dried under vacuum. Yield 70% .

Anal. Found (Calcd. for $C_{10}H_8N_2NiWS_4$): C, 22.95 (22.78); H, 1.69 (1.52); N, 5.42 (5.32); Ni, 10.94 (11.14); S, 24.16 (24.3).

3.7.4 Preparation of $[(o\text{-phen})NiS_2MoS_2]$

$NiCl_2 \cdot 6H_2O$ (240 mg, 1 mmol) and 1,10-phenanthroline monohydrate (400 mg, 2 mmol) were dissolved in ethanol (25 mL), to give the lilac blue bis complex. The solution was added in drops to a solution of ammonium tetrathiotungstate (350 mg, 1 mmol) in water (20 mL) with stirring. A yellow precipitate separated out immediately and the reaction mixture was further stirred for 1 h and filtered. The yellow product was washed well with water, ethanol and ether and dried under vacuum. Yield 90%.

Anal. Found (Calcd. for $C_{12}H_8N_2NiWS_4$): C, 26.52 (26.15); H, 1.72 (1.45); N, 5.31 (5.08); Ni, 10.47 (10.66); S, 23.02 (23.24).

3.7.5 Preparation of $[(bipy)NiS_2MoOS]$

An ethanolic solution (25 mL) of dichlorobis(bipyridine) nickel(II) was prepared from $NiCl_2 \cdot 6H_2O$ (240 mg, 1 mmol) and 2,2'-bipyridine (320 mg, 2 mmol). The lilac blue solution was added in drops to a solution of cesium oxotriethiomolybdate (475 mg, 1 mmol) in water (20 mL) with stirring. An orange precipitate separated out immediately and the reaction mixture was further stirred for 1 h and filtered. The orange product was isolated by filtration washed well with water, ethanol and ether and dried under vacuum. Yield 90%.

Anal. Found (Calcd. for $C_{10}H_8N_2NiMoOS_3$): C, 28.67 (28.39); H, 1.98 (1.89); N, 6.43 (6.62); Ni, 13.68 (13.89); S, 22.54 (22.71).

3.7.6 Preparation of [(o-phen)NiS₂MoOS]

The procedure employed for the synthesis of this complex is similar to that of its bipyridine analog. 1,10-phenanthroline monohydrate (400 mg, 2mmol) was used instead of 2,2-bipyridine. The light brown product thus obtained was washed well with water, ethanol and ether and dried in vacuo. Yield 80% .

Anal. Found (Calcd. for C₁₂H₈N₂NiMoOS₃): C, 32.46 (32.24); H, 1.95 (1.79); N, 6.45 (6.27); Ni, 13.04 (13.14); S, 21.25 (21.49).

3.7.7 Preparation of [(bipy)NiS₂WOS]

An ethanolic solution (25 mL) of dichlorobis(bipyridine) nickel(II) was prepared from NiCl₂.6H₂O (240 mg, 1 mmol) and 2,2'-bipyridine (320 mg, 2 mmol). The lilac blue solution was added in drops to a solution of ammonium oxotritungstate (330 mg, 1 mmol) in water (20 mL) with stirring. A yellow precipitate separated out immediately and the reaction mixture was further stirred for 1 h and filtered . The yellow product was isolated by filtration washed well with water, ethanol and ether and dried under vacuum. Yield 90% .

Anal. Found (Calcd. for C₁₀H₈N₂NiWOS₃): C, 23.72 (23.50); H, 1.78 (1.57); N, 5.77 (5.48); Ni, 11.22 (11.49); S, 18.53 (18.8).

3.7.8 Preparation of [(o-phen)NiS₂WOS]

The procedure employed for the synthesis of this complex is similar to that of its bipyridine analog. 1,10-phenanthroline monohydrate (400 mg, 2 mmol) was used instead of 2,2-bipyridine. The light yellow product thus obtained was washed well with water, ethanol and ether and dried in vacuo. Yield 80% .

Anal. Found (Calcd. for $C_{12}H_8N_2NiWOS_3$): C, 27.21 (26.93); H, 1.82 (1.5); N, 5.57 (5.24); Ni, 10.58 (10.98); S, 17.67 (17.95).

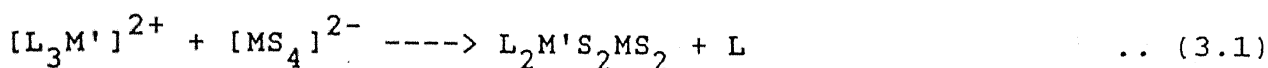
3.8 SYNTHETIC ASPECTS AND REACTIVITY OF THE COMPLEXES:

The complexes prepared in this work are essentially 1:1 neutral bimetallic complexes, having one equivalent of the bivalent transition metal and one equivalent of the thiometallate. All the syntheses have been carried out in aqueous-alcoholic medium and the isolated complexes are quite stable. The iron-thiometallate complexes are all red in color while the color of the other complexes range from orange to yellow. The neutral complexes are soluble only in solvents like DMF, NMF, or DMSO. The hexacoordinate nickel(II) complexes are not very soluble.

The reaction of the thiometallates with bivalent metal ions in aqueous medium lead to the formation of a mixture of amorphous metal sulfides [155]. However, in the presence of cations like $[XPh_4]^+$ ($X=P, As$) the sulfide formation can be prevented and tetracoordinated bis(thiometallato) complexes are formed [11,12]. In the case of Fe(II) even the use of $[PPh_4]^+$ does not afford any discrete complexes but gives only polymeric species. The polymerisation and sulfide formation tendency can be effectively prevented by the use of coligands like aromatic diimines, resulting in the formation of discrete sulfur bridged bimetallic complexes. In all the complexes reported in this work the aromatic diimines are coordinated to the bivalent metal. From the analytical data it is clear that all these divalent metal complexes are hexa-

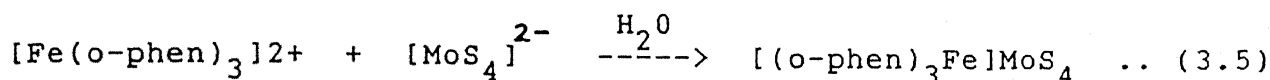
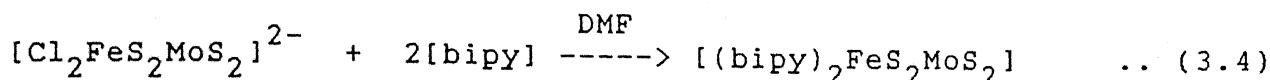
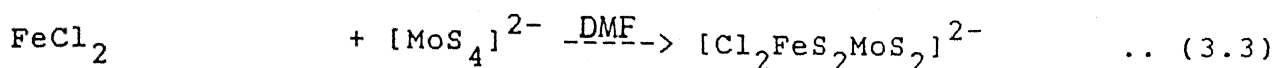
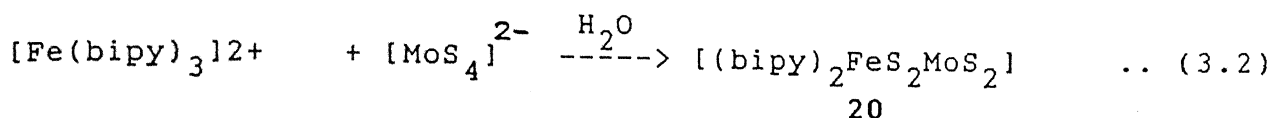
coordinate, bound by two bidentate N-donor ligands and a bidentate thiometallate. In the case of Ni(II), in addition to the hexacoordinate complexes, we have also prepared tetracoordinate mixed ligand complexes.

The formation of the hexacoordinate mixed ligand complex can be thought of as a simple ligand displacement reaction at the bivalent metal site wherein one of the bidentate aromatic heterocycle has been exchanged for the thiometallate as in eq (3.1),



where $M' = \text{Mn, Fe, Co, Ni}$; $M = \text{Mo, W}$; $L = \text{aromatic diimine}$. The neutral bis(diimine) complexes of iron(II), $[\text{Fe}L_2X_2]$ are well documented in the literature [159,160] and they are generally prepared from the tris(diimine) complexes by substitution with suitable ligand. The iron-thiometallate complexes prepared by us (Section 3.4) are the first example of hexacoordinate iron complexes in Fe-Mo/W chemistry.

The reaction of $[\text{Fe}(\text{bipy})_3]^{2+}$ ($\text{bipy} = 2,2'\text{-bipyridine}$) with thiometallate results in the formation of the sulfur bridged, neutral bimetallic complexes, whereas the reaction of $[\text{Fe}(\text{o-phen})_3]^{2+}$ gives only the $[\text{Fe}(\text{o-phen})_3]^{2+}$ ($\text{o-phen} = 1,10\text{-phenanthroline}$) salt of the thiometallate. The formation of the salt-like species is intriguing since neutral complexes of the type $[\text{Fe}(L_2)X_2]$ ($L = 2,2'\text{-bipyridine}$ or $1,10\text{-phenanthroline}$; $X = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{SCN}^-, \text{CN}^-$) are known. The formation of the sulfur-bridged bimetallic complex can be accomplished in both aqueous and non-aqueous medium as follows:



The formation of $[(\text{bipy})_2\text{FeS}_2\text{MoS}_2]_{20}$ [eq (3.2)] is similar to the aqueous preparation of bis(diimine) complexes, from tris(diimine) complexes, reported by Schilt and Fritsch [167]. The first step in the DMF method for the isolation of $[(\text{bipy})_2\text{FeS}_2\text{MoS}_2]$ involves the generation of the well known complex, $[\text{Cl}_2\text{FeS}_2\text{MoS}_2]^{2-}$. The second step involves the exchange of the chloride ligands for bipyridine. It is interesting to note that two equivalents of (bipy) are taken up to produce 20. The complexes isolated from both the methods exhibit identical X-ray powder pattern. The complex $[\text{Cl}_2\text{FeS}_2\text{MoS}_2]^{2-}$ is known to undergo ligand displacement reactions and the $\{\text{Fe}(\mu\text{-S})_2\text{Mo}\}$ core is inert under these conditions [106]. Hence, these reactions are straight forward and can be understood in terms of simple ligand exchange at the bivalent metal site. The use of other thiometallates like $[\text{WS}_4]^{2-}$, $[\text{MoOS}_3]^{2-}$ and $[\text{WOS}_3]^{2-}$ gives the corresponding sulfur bridged bimetallic complexes.

The formation of the salt $[\text{Fe}(\text{o-phen})_3]\text{MoS}_4$ [eq(3.5)] is a simple cation exchange reaction. The difference in the reactivity between (o-phen) and (bipy) is not surprising, as (o-phen) is known to behave differently in $[\text{Fe-M-S}]$ systems. To account for the disappearance of the EPR signal of the Fe-Mo-co on treatment with (o-phen), the reaction of (o-phen) with various $[\text{Fe-Mo-S}]$ systems were carried out and it was found that in all the cases iron was removed completely (Table 3.1) [162]. (o-phen) has a high affinity for iron as is seen in the reaction of (o-phen) with the reduced cubane cluster $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$. From Table 3.1, it is clear that (o-phen) can even bind the iron from the well known inert core, $\{\text{Fe}(\mu\text{-S})_2\text{Mo}\}$ in $[\text{Cl}_2\text{FeS}_2\text{MoS}_2]^{2-}$, whereas $\{\text{Fe}(\mu\text{-S})_2\text{Mo}\}$ retains its identity with (bipy). It is also to be noted that the EPR signal of Fe-Mo-co does not vanish when treated with (bipy).

All attempts to synthesize the complex $[(\text{o-phen})_2\text{FeS}_2\text{MoS}_2]$ were not successful. The addition of Fe(II) to a solution containing both $[\text{MoS}_4]^{2-}$ and (o-phen), or the use of excess Fe(II) than that is needed for the reaction, the use of reduced amounts of (o-phen) resulted in the formation of only the salt-like species. The same behavior was observed when other thiometallates were used. The reaction of (o-phen) with a preformed core like $\{\text{Fe}(\mu\text{-S})_2\text{Mo}\}$ is known to remove all the Fe as the $[\text{Fe}(\text{o-phen})_3]^{2+}$ [162]. The reason for the formation of $[\text{Fe}(\text{o-phen})_3]\text{MS}_4$ as compared to $[(\text{bipy})_2\text{FeS}_2\text{MS}_2]$ may then be due to the high formation

Table 3.1

Reaction of Mo-Fe-S clusters with 1,10-phenanthroline [162]

Complex	% Fe observed as		% (MoS ₄) ²⁻ recovered
	[Fe(o-phen) ₃] ²⁺		
	Before O ₂	After O ₂	
[Fe ₄ S ₄ (SPh) ₄] ²⁻	89	95	N/A
[Mo ₂ Fe ₆ S ₈ (SPh) ₉] ³⁻	99	100	74
[MoS ₄ FeCl ₂] ²⁻	100	100	100
[Fe(MoS ₄) ₂] ³⁻	<10	100	50
FeMoco	8-30	100	ND

N/A not available

ND not determined

constants of $[\text{Fe}(\text{o-phen})_3]^{2+}$ ($K_3=10^{10}$) as opposed to a lower value for $[\text{Fe}(\text{bipy})_3]^{2+}$ ($K_3=8 \times 10^7$). Thus, no ligand exchange takes place with (o-phen) and the tris(phenanthroline)iron(II) simply acts as a bulky cation to trap the thiometallate.

Complexes like $[\text{FeCl}_2\text{MoS}_4]^{2-}$ and $[(\text{FeCl}_2)_2\text{MS}_4]^{2-}$ ($\text{M}=\text{Mo}, \text{W}$) can be easily prepared by the reaction of anhydrous FeCl_2 with thiometallates in non-aqueous solvents. All attempts to synthesize the analogous Co and Ni complexes by the reaction of the anhydrous chlorides of Co or Ni were not successful and only bis(thiometallato) complexes are formed. Thus Co and Ni are different from Fe in their reactivity towards thiometallates. But, the reactions of $[\text{M}'\text{L}_3]^{2+}$ ($\text{M}=\text{Co}, \text{Ni}$; $\text{L}=\text{aromatic diimine}$) with thiometallates results in the formation of simple 1:1 complexes which are isostructural with the Fe-thiometallate complexes. In the case of Ni(II), the use of neutral complexes like $[\text{NiL}_2\text{Cl}_2]$ result in the formation of tetracoordinate complexes. Thus, the reaction of aromatic diimine complexes with thiometallates appears to be a general reaction for the formation of bimetallic sulfur-bridged complexes. The generality of this reaction has been tested with Mn(II) for which no thiometallato complexes are known. The reaction of MnCl_2 with $[\text{MoS}_4]^{2-}$ gives only a mixture of amorphous sulfides. The general procedure for the preparation of bis(thiometallato) complexes eq (1.15) does not give rise to any Mn-thiometallate complexes.

A recent attempt by Manoli and coworkers [57] to synthesize the complex $[\text{Mn}(\text{WS}_4)_2]^{2-}$ from a non-aqueous medium by the reaction of $(\text{PPh}_4)_2\text{WS}_4$ with MnCl_2 has resulted in the formation

of a binary W-S complex $[W_2S_{11}]^{2-}$. The role of Mn to bring about the aforesaid transformation has not been clearly understood. However, the reaction of the aromatic diimine complexes of Mn(II) with thiometallates proceeds readily and hexacoordinate Mn(II) complexes are formed. These reactions clearly indicate that aromatic diimines are stable coligands and the use of coligands in the syntheses of thiometallato complexes will give rise to 1:1 complexes. The Mn-thiometallate complexes reported in this work are the first example of a Mn-Mo/W complex stitched by sulfur bridges.

The reactivity of the complexes $[L_2FeS_2MS_2]$ (M=Mo,W) with i) excess thiometallate and ii) with $FeCl_2$ were investigated by us to see whether a second thiometallate can be coordinated to the bivalent metal at the expense of an organic ligand resulting in the formation of $[LFe(WS_4)_2]^{2-}$ and to incorporate a third metal thus making use of the terminal sulfurs in the starting 1:1 complex. In both the cases the starting materials were only recovered. The attempted synthesis of $[LFe(WS_4)_2]^{2-}$ from $[Fe(WS_4)_2]^{2-}$ by reacting it with bipyridine results exclusively in the formation of the neutral complex $[L_2Fe(WS_4)]$. The reaction of $[L_2FeS_2MS_2]$ with $FeCl_2$ in DMF does not result in the formation of the trinuclear complex. This result reinforces the earlier observation that the coordinated thiometallate does not have high affinity for a second metal ion [74].

The attempted synthesis of $[\text{Mn}(\text{MS}_4)_2]^{2-}$ by reacting $[\text{L}_2\text{MnMoS}_4]$ with excess thiometallate did not result in the formation of the bis(thiometallato) complex. In the synthesis of the Mn-thiometallate complexes, irrespective of whether excess thiometallate or reduced amounts of bipyridine was used the only isolable product has always been the hexacoordinate complex $[\text{L}_2\text{MnS}_2\text{MS}_2]$ which clearly indicates the high formation tendency of these complexes.

CHAPTER 4

STRUCTURAL ASPECTS OF THE SYNTHESIZED COMPLEXES

The bimetallic complexes have been studied by vibrational, electronic, and electron paramagnetic resonance spectroscopy, magnetic susceptibility measurements, cyclic voltammetry and X-ray powder diffraction. The results of these studies are presented below.

4.1. Vibrational spectroscopy:

The IR spectra of the complexes were recorded on a Perkin-Elmer model 580 infrared grating spectrophotometer. The samples were prepared as CsI pellets and referenced to polystyrene bands.

From the analytical data of the synthesized complexes it is evident that one equivalent of thiometallate and two equivalents of aromatic diimine are present per bivalent metal. In the case of Ni(II), another series of complexes having one equivalent of thiometallate and one equivalent of the organic ligand per nickel have also been synthesized. The mode of coordination of the thiometallate ligands in these complexes can be obtained by a careful analysis of the infrared spectra of these complexes. The usefulness of infrared spectroscopy in elucidating the structures of thiometallato complexes has already been mentioned in the introductory chapter [Table 1.4, Fig. 1.8].

When binuclear complexes are formed the tetrathiometallate ligands function as one-fold bidentate ligand leaving a pair of terminal M-S bonds leading thereby to the reduction of the local

symmetry of the tetrathiomallate ligand from T_d to C_{2v} . The correlation of $\nu(M-S)$ vibrations of the MS_4 group in these symmetries are given below:

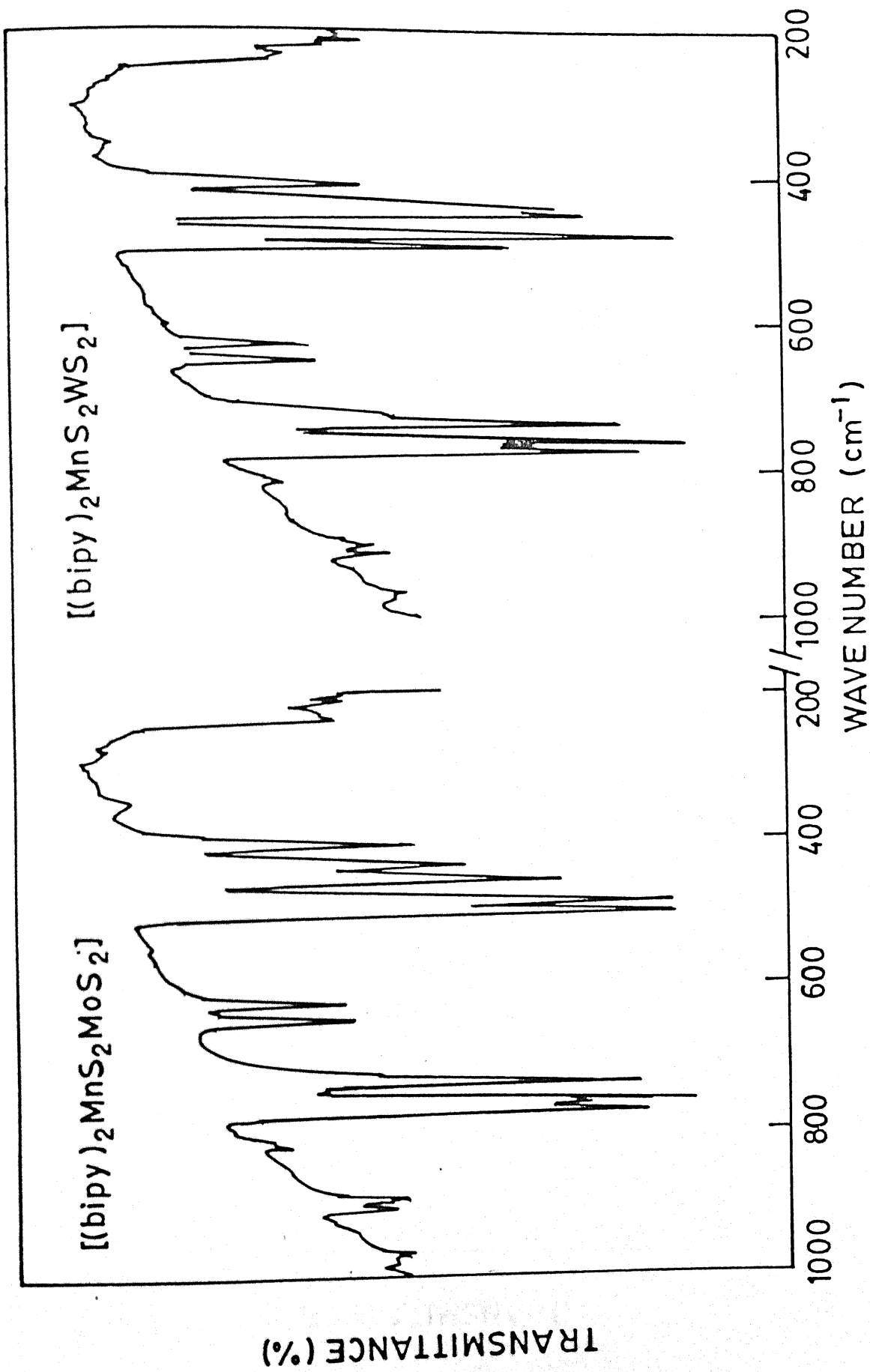
T_d	C_{2v}
$A_1(R)$	$A_1(IR,R)$
$E(R)$	$A_1(IR,R) + A_2(R)$
$E_2(IR,R)$	$A_1(IR,R) + B_1(IR,R) + B_2(IR,R)$

Thus, the $\nu_1(A_1)$ vibration of the free $[MS_4]^{2-}$ ion retains its totally symmetric nature even after coordination and this vibration is of the ν_s type. However, the asymmetric vibration $\nu_3(E_2)$ is split. In practice, the terminal $(M=S)$ groups are characterized by one or two vibrational frequencies between 480-510 cm^{-1} and the bridging $(M-S_{br})$ groups by frequencies between 430-460 cm^{-1} . For complexes having $[MOS_3]^{2-}$ ligands a characteristic band for the $\nu(MO_{term})$ vibration is observed in the region 850-950 cm^{-1} . The thiomallate complexes reported in this work have the aromatic diimines 2,2'-bipyridine (bipy) and 1,10-phenanthroline (o-phen) as coligands. Since these organic ligands have no absorption in the 430-520 cm^{-1} region the identification and assignment of the metal sulfur vibrations becomes easy.

The salt $[Fe(o-phen)_3]MoS_4$ shows a single band $\nu(MS_{as})$ in its IR spectrum around 480 cm^{-1} and the characteristic bands of coordinated (o-phen). The single band is characteristic of free thiomallate and thus the coordination of $(MoS_4)^{2-}$ to Fe through sulfur is ruled out in this complex. The coordination, if occurs would increase the coordination number of Fe to 8 which is seldom

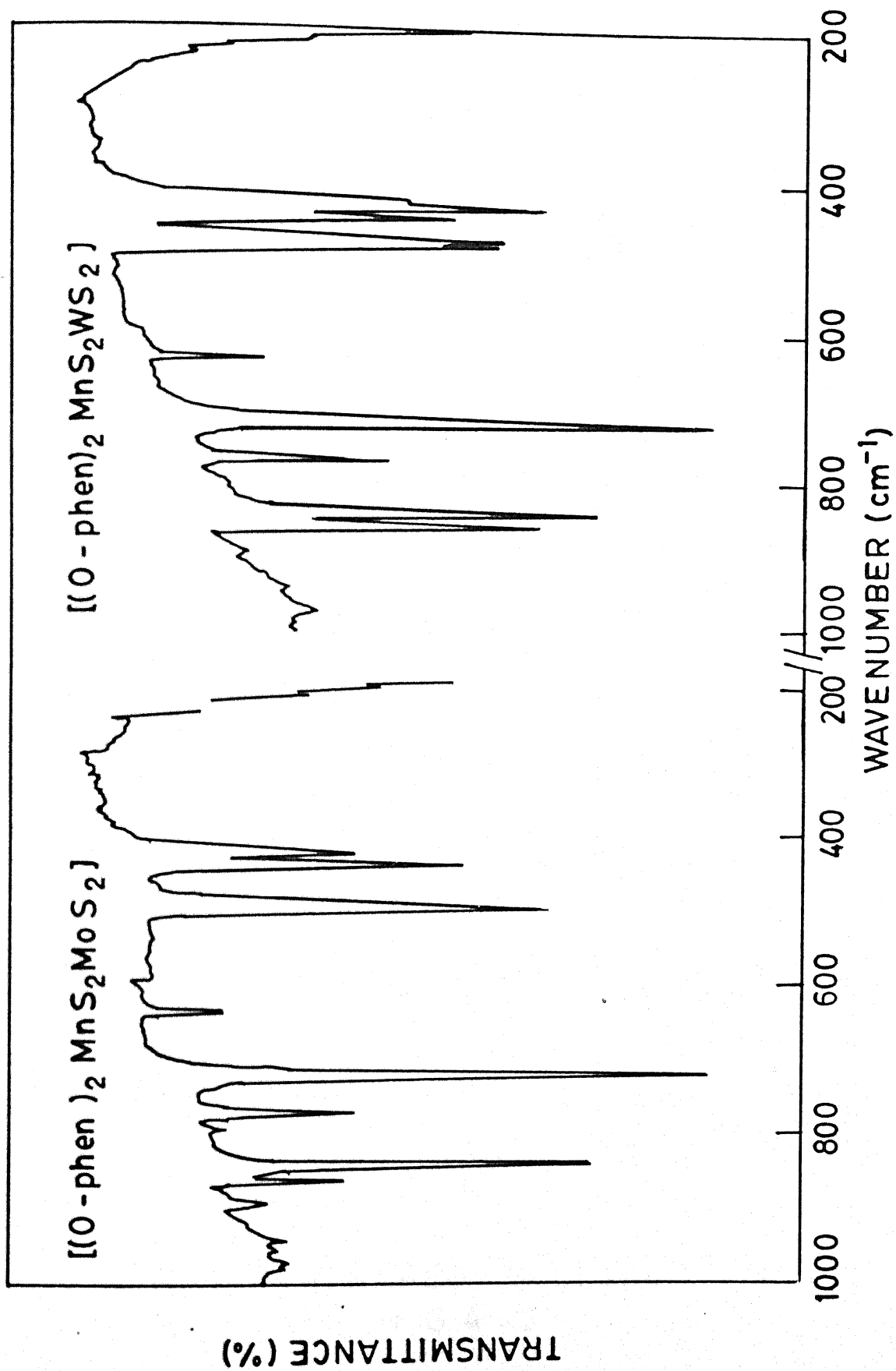
encountered in iron chemistry. The IR spectra of all the iron-thiometallate complexes synthesized from $[\text{Fe}(\text{o-phen})_3]^{2+}$ clearly indicate that all these compounds are simple salts. In all the other complexes, the IR spectra are characteristic of the coordination of $[\text{MS}_4]^{2-}$ units resulting in the formation of the sulfur-bridged bimetallic unit $\{\text{M}'(\mu\text{-S})_2\text{M}\}$ ($\text{M}=\text{Mo}, \text{W}$; $\text{M}'=\text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$). The presence of the bimetallic unit $\{\text{M}'(\mu\text{-S})_2\text{M}\}$ can be further substantiated from the IR spectra of the corresponding oxotrithiometallato complexes.

The infrared spectra of the synthesized complexes are depicted in Figs. 4.1.1 to 4.1.10. The assignments to the $\nu(\text{MS}_{\text{term}})$, $\nu(\text{MS}_{\text{br}})$, and $\nu(\text{MO}_{\text{term}})$ vibrations are listed in Table 4.1. The infrared spectra of the tetrathiometallato complexes [Figs. 4.1.1 to 4.1.5] show the characteristic splitting nature of the free thiometallate bands which results upon complexation. From the data (Table 4.1), it is very clear that the spectra of the thiometallato complexes are in accordance with the theoretical predictions. The terminal $\text{M}=\text{S}$ stretch occurs at a higher frequency than that of the free thiometallate while the bridging $\text{M}-\text{S}$ stretch occurs at a lower frequency. A common trend that has been observed in many tetrathiometallato complexes reported till date [12] is the appearance of a single band for the bridging $\text{M}-\text{S}$ vibration, two bands for the terminal $\text{Mo}=\text{S}$ vibration and a single band for the terminal $\text{W}=\text{S}$ vibration in their IR spectra. However, the $\nu(\text{WS}_{\text{term}})$ vibration has been resolved into two closely spaced bands by high resolution technique [143]. The IR spectra of the Mn-thiometallate



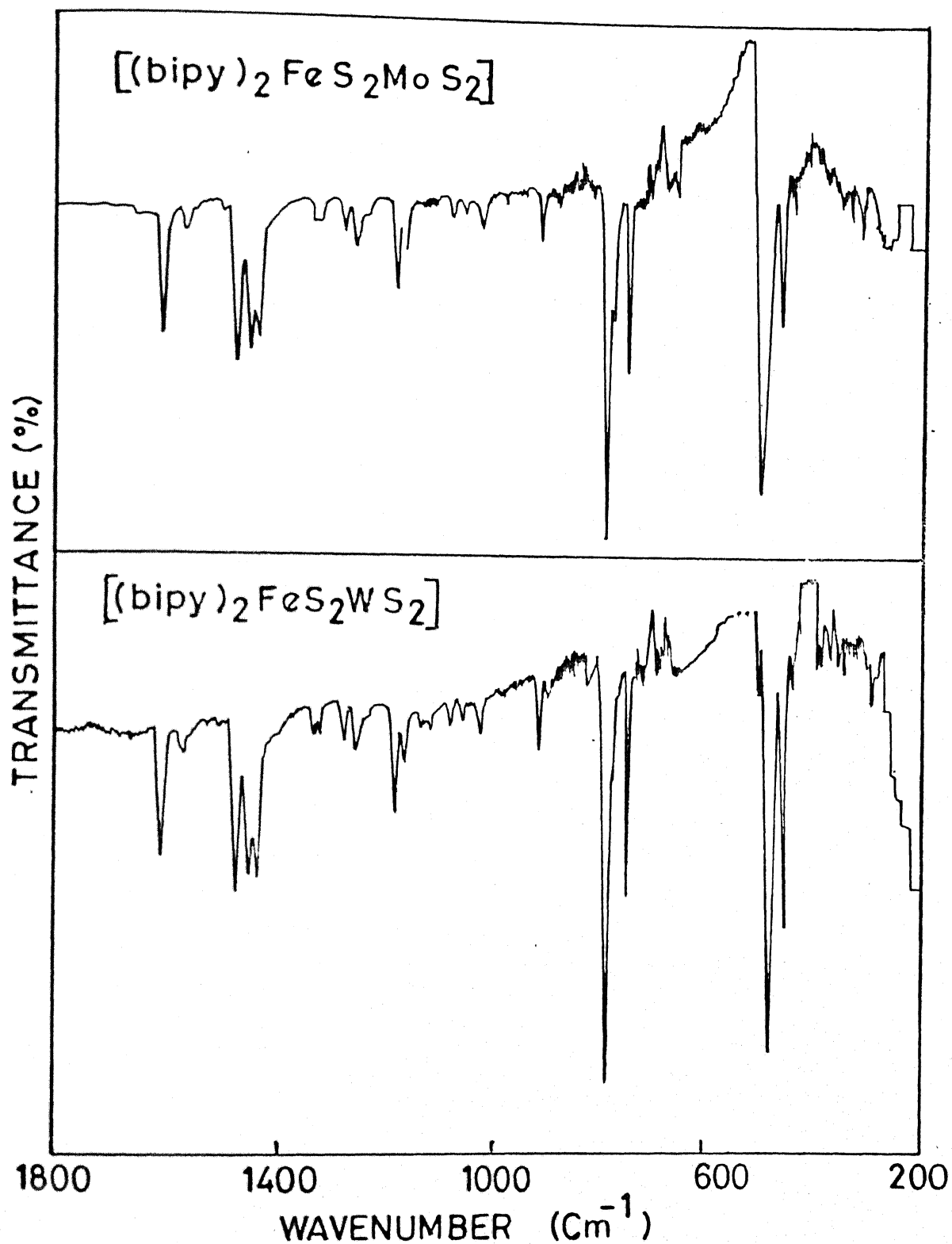
INFRARED SPECTRA

FIG. 4.1.1



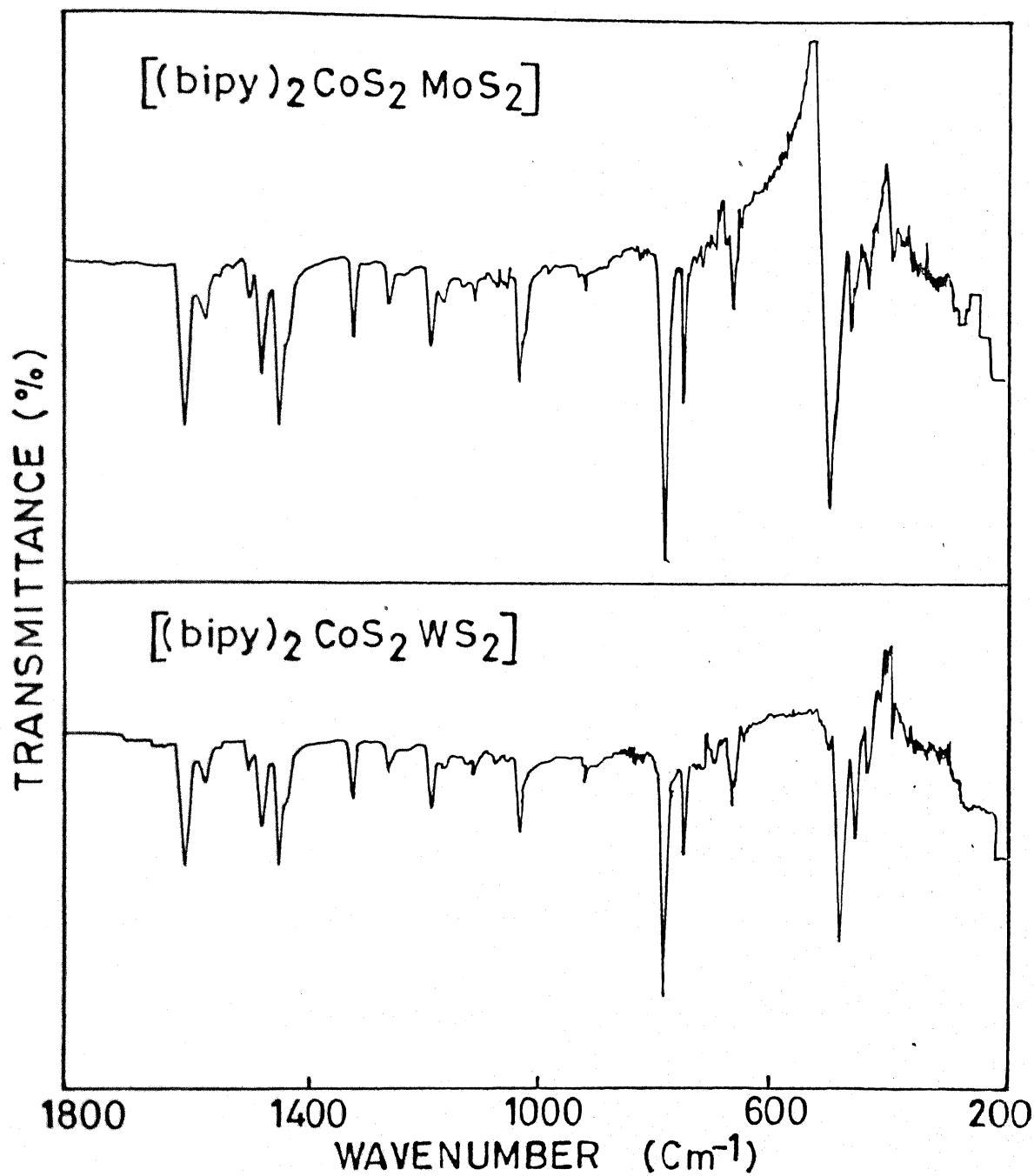
INFRARED SPECTRA

FIG. 4.1.2



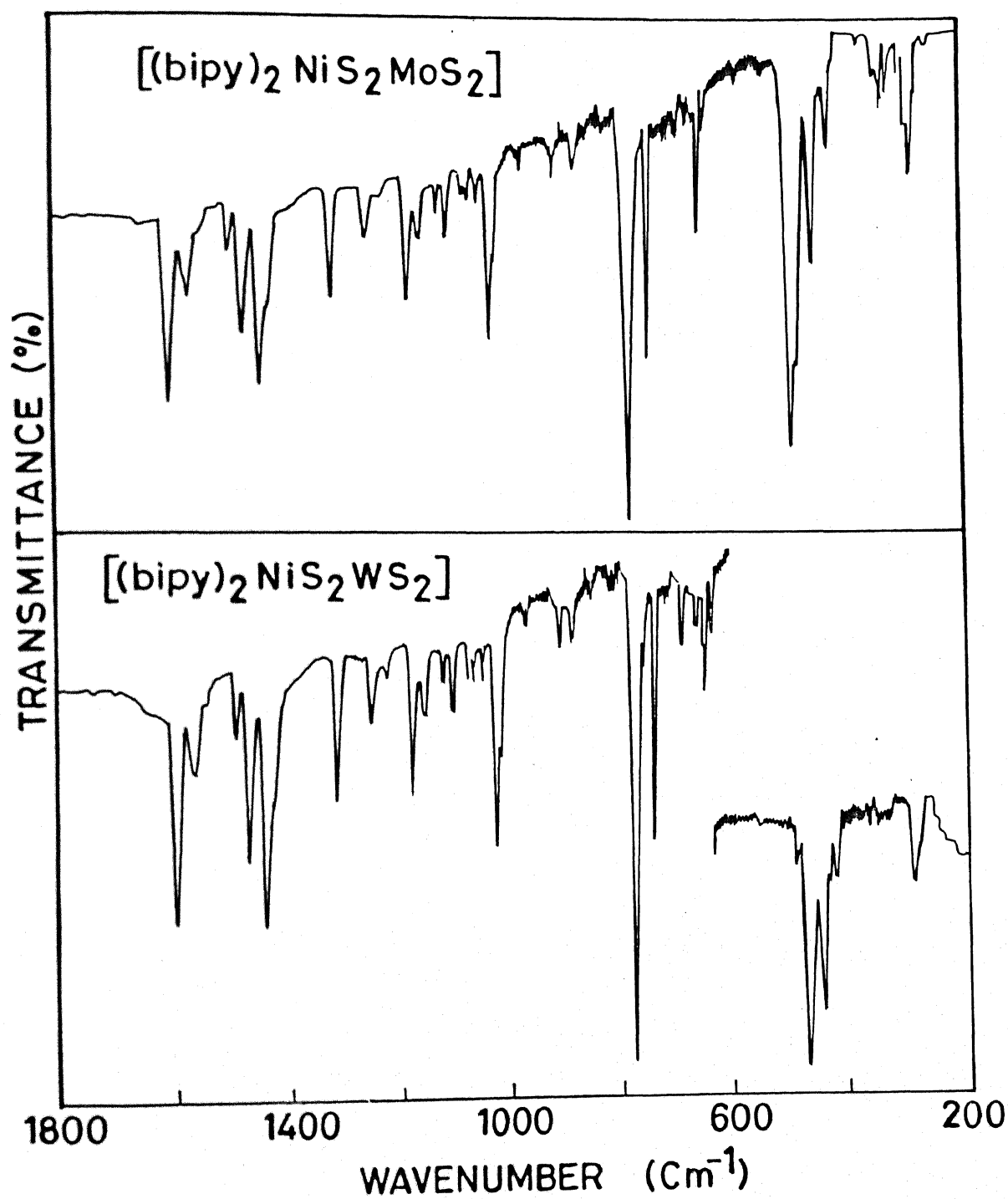
INFRARED SPECTRA

FIG. 4.1.3



INFRARED SPECTRA

FIG. 4.1.4



INFRARED SPECTRA

FIG. 4.1.5

Table 4.1

Important vibrational frequencies of $[L_n M'(MS_4)]$ complexes

Complex	$\nu(MO_{term})$	$\nu(MS_{term})$ cm-1	$\nu(MS_{br})$
$(NH_4)_2 MoS_4$	---	480	---
$[(bipy)_2 MnS_2 MoS_2]$	---	505, 490	455, 435
$[(bipy)_2 MnS_2 WS_2]$	---	490, 480	450, 440
$Cs_2 MoOS_3$	862	480	---
$[(bipy)_2 MnS_2 MoOS]$	890	490	460, 440
$[(bipy)_2 MnS_2 WOS]$	910, 855	480	440
$[(o-phen)_2 MnS_2 MoS_2]$	---	500, 495	440, 430
$[(o-phen)_2 MnS_2 WS_2]$	---	485, 475	450, 435
$[(o-phen)_2 MnS_2 MoOS]$	890	500	455, 430
$[(o-phen)_2 MnS_2 WOS]$	890	480	450
$[(o-phen)_3 FeMoS_4]$	---	475	---
$[(o-phen)_3 FeWS_4]$	---	458	---
$[(bipy)_2 FeS_2 MoS_2]$	---	490, 485	455
$[(bipy)_2 FeS_2 WS_2]$	---	475	450
$[(bipy)_2 FeS_2 MoOS]$	873	490	455
$[(bipy)_2 FeS_2 WOS]$	890	485, 470	450
$[(bipy)_2 CoS_2 MoS_2]$	---	490	460
$[(bipy)_2 CoS_2 WS_2]$	---	475	450
$[(bipy)_2 CoS_2 MoOS]$	870	490	460
$[(bipy)_2 CoS_2 WOS]$	895	485, 470	450

contd.

Complex	$\nu(\text{MO}_{\text{term}})$	$\nu(\text{MS}_{\text{term}})$ cm-1	$\nu(\text{MS}_{\text{br}})$
$[(\text{bipy})_2\text{NiS}_2\text{MoS}_2]$	---	490,475	450
$[(\text{bipy})_2\text{NiS}_2\text{WS}_2]$	---	470	440
$[(\text{bipy})_2\text{NiS}_2\text{MoOS}]$	870	485	455
$[(\text{bipy})_2\text{NiS}_2\text{WOS}]$	890	470	445
$[(\text{o-phen})_2\text{NiS}_2\text{MoS}_2]$	---	485	445
$[(\text{o-phen})_2\text{NiS}_2\text{WS}_2]$	---	470	440
$[(\text{o-phen})_2\text{NiS}_2\text{MoOS}]$	875	485	455
$[(\text{o-phen})_2\text{NiS}_2\text{WOS}]$	895	465	445
$[(\text{bipy})\text{NiS}_2\text{MoS}_2]$	---	510,500	470
$[(\text{bipy})\text{NiS}_2\text{WS}_2]$	---	500,490	460
$[(\text{bipy})\text{NiS}_2\text{MoOS}]$	910	505	470,450
$[(\text{bipy})\text{NiS}_2\text{WOS}]$	920	490	460,445
$[(\text{o-phen})\text{NiS}_2\text{MoS}_2]$	---	505	470
$[(\text{o-phen})\text{NiS}_2\text{WS}_2]$	---	485	460
$[(\text{o-phen})\text{NiS}_2\text{MoOS}]$	905	500	475
$[(\text{o-phen})\text{NiS}_2\text{WOS}]$	920	485	460

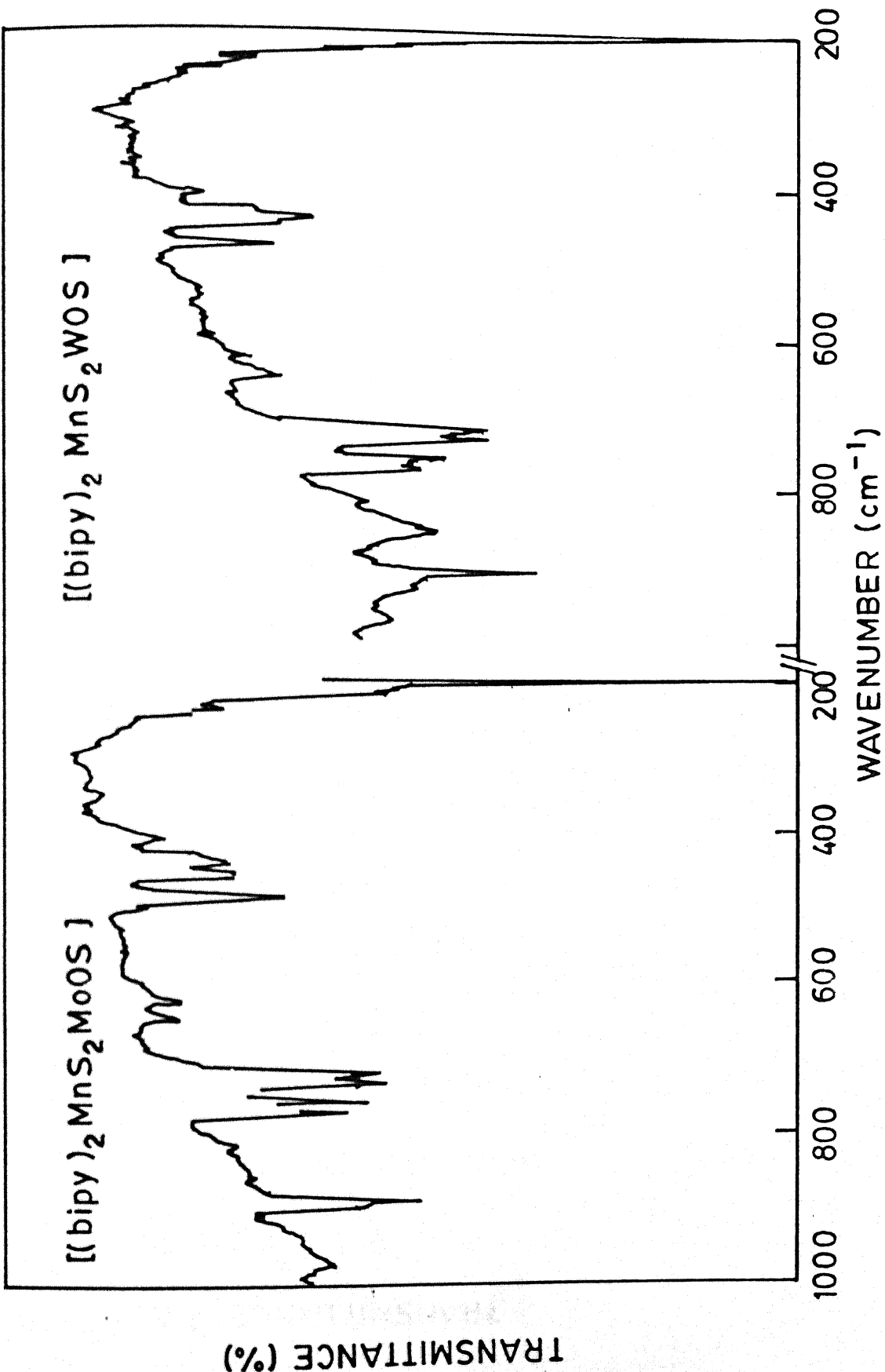
L = 2,2'-bipyridine, 1,10-phenanthroline

M' = Mn, Fe, Co, Ni; M = Mo, W

term = terminal ; br = bridging

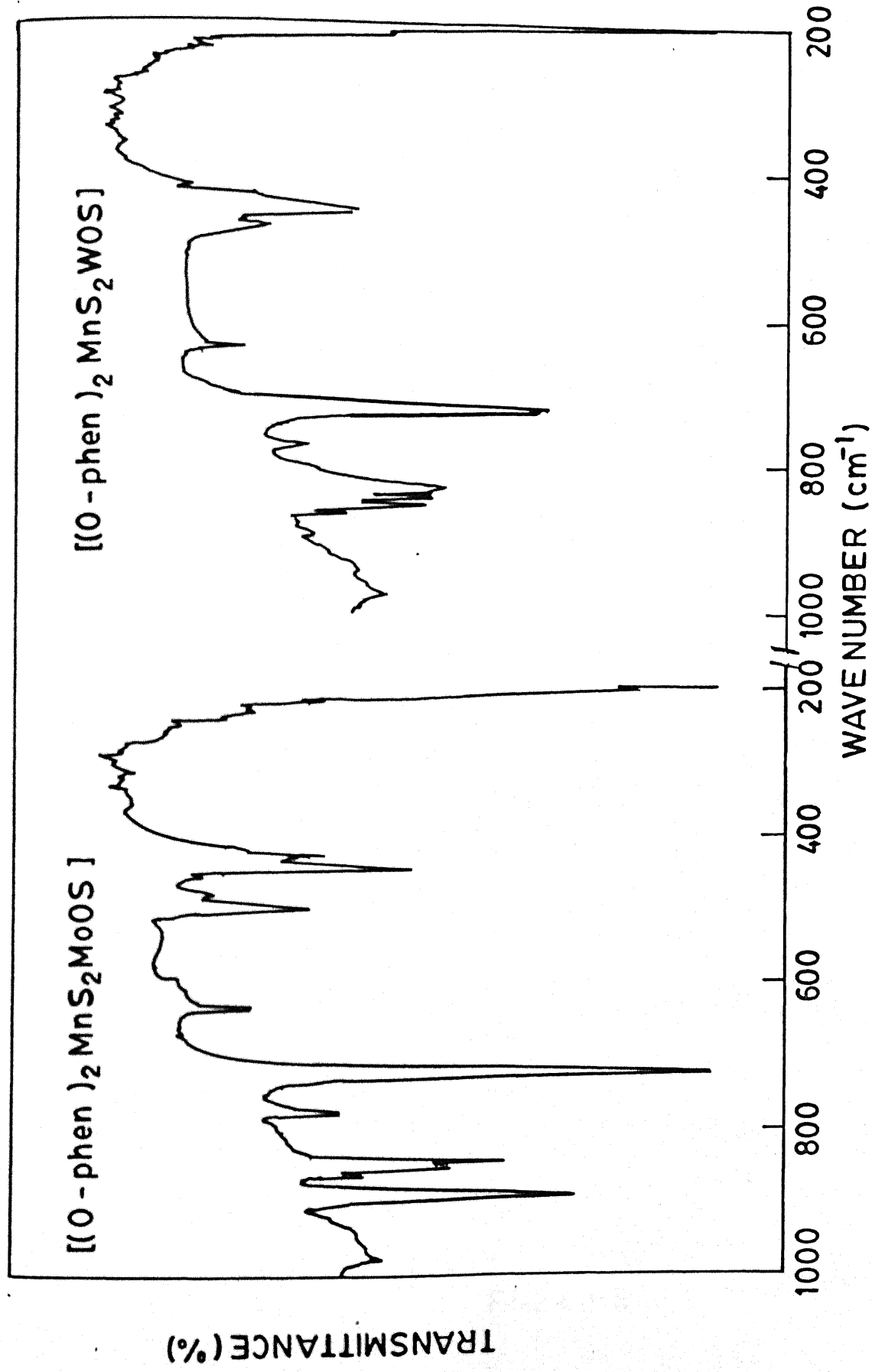
complexes are striking, since they exhibit four distinct bands in the $400\text{--}500\text{ cm}^{-1}$ region two of which can be assigned to $\nu(\text{MS}_{\text{term}})$ and the other two at lower frequency to $\nu(\text{MS}_{\text{br}})$ vibrations. The $\nu(\text{WS}_{\text{term}})$ and $\nu(\text{WS}_{\text{br}})$ vibrations generally appear at a lower frequency compared to $\nu(\text{MoS}_{\text{term}})$ and $\nu(\text{MoS}_{\text{br}})$ in the corresponding Mo analogs and these observations are consistent with the expected trend. Small spectral changes are observed in the M-S-M' bridge vibrations as the mass of M' is increased from Mn to Ni and that of Mo to W but the shifts are less than predicted by simple reduced mass calculations, presumably due to change in force constants as well as mixing of several vibrational modes as indicated by normal coordinate analysis [143-145]. The two other important vibrations of these complexes are $\nu(\text{M}'\text{S})$ and $\nu(\text{M}'\text{N})$. These vibrations generally appear as weak bands in the lower end of the spectrum far below 400 cm^{-1} . The Mn-N stretch occurs around 225 cm^{-1} for the $[\text{Mn}(\text{bipy})_3]^{2+}$ complex [142]. Based on this, a band around 235 cm^{-1} has been tentatively assigned to $\nu(\text{MnN})$ and a band at 350 cm^{-1} has been tentatively assigned to $\nu(\text{MnS})$. In some of the spectra, the region below 400 cm^{-1} is not well resolved, thus making the assignments of the weak $\nu(\text{M}'\text{N})$ and $\nu(\text{M}'\text{S})$ bands very difficult. In the nickel complexes $[(\text{bipy})_2\text{NiMS}_4]$ the band around 290 cm^{-1} can be tentatively assigned to $\nu(\text{NiN})$.

The IR spectra of all the oxotrithiometallato complexes exhibit an intense band in the $850\text{--}950\text{ cm}^{-1}$ region [Figs. 4.1.6-4.1.10], which is very characteristic of $\nu(\text{MO}_{\text{term}})$ vibration. The presence of this band in addition to the $\nu(\text{MS}_{\text{term}})$ and



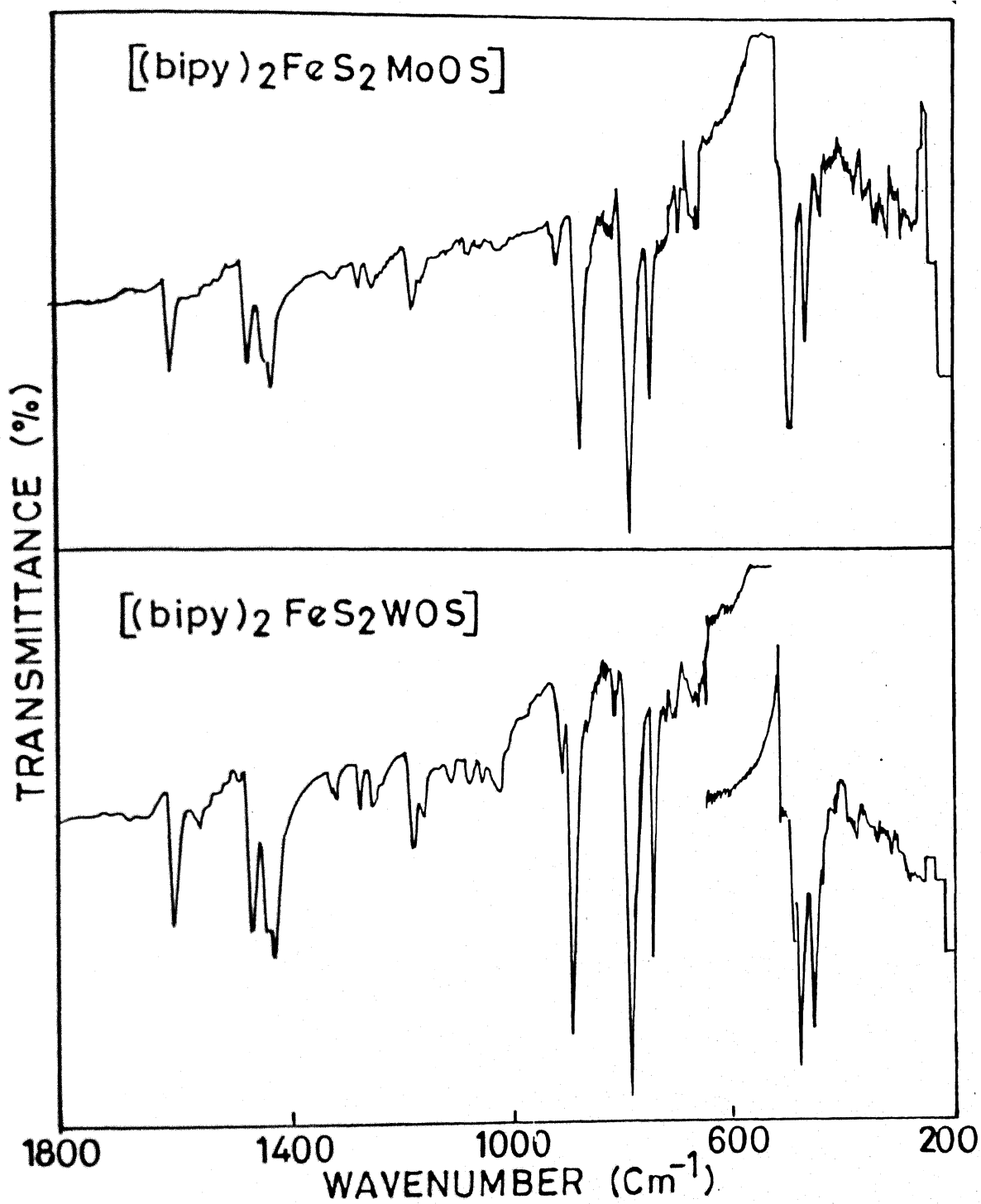
INFRARED SPECTRA

FIG. 4.1.6



INFRARED SPECTRA

FIG. 4.1.7



INFRARED SPECTRA

FIG. 4.1.8

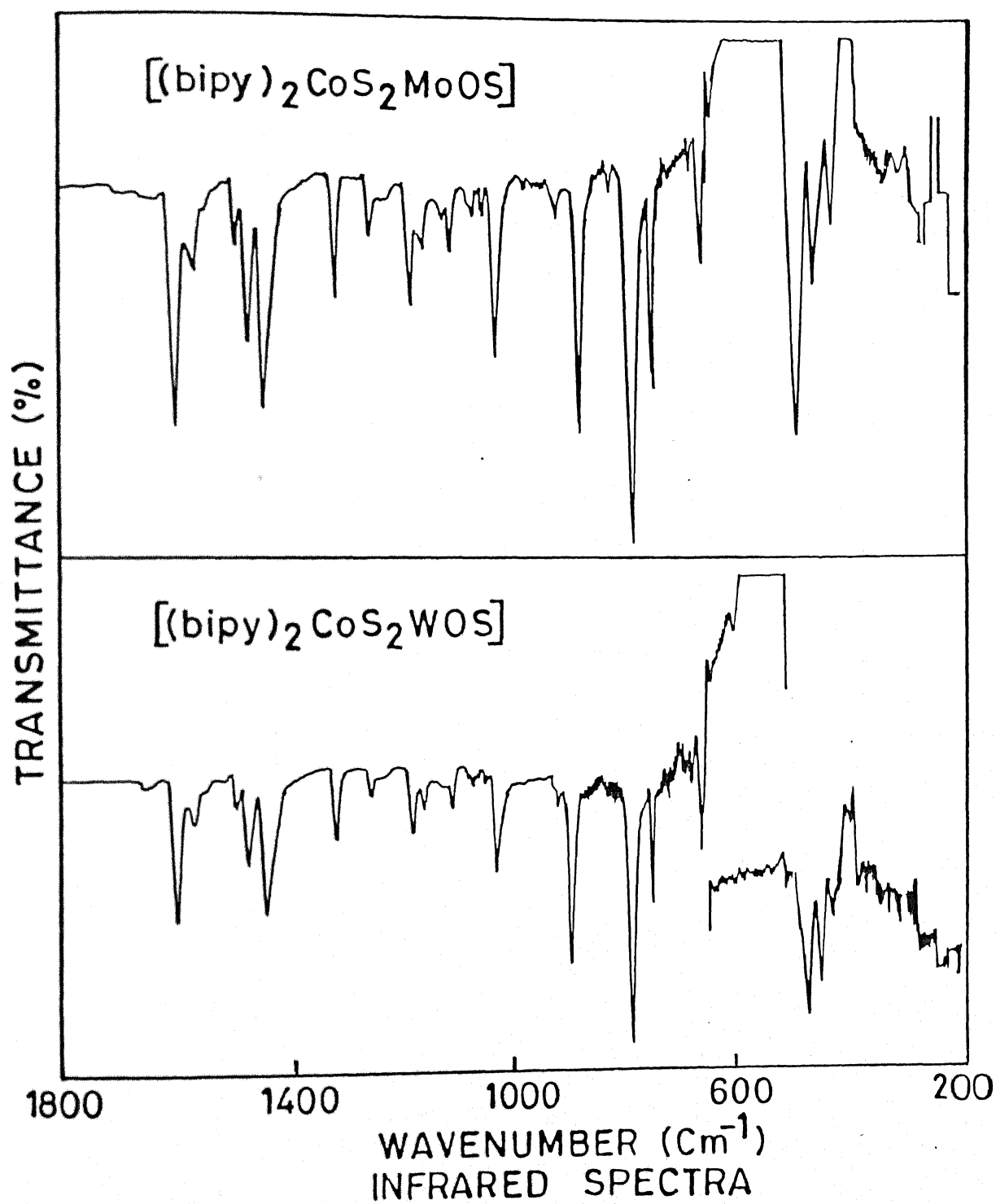


FIG. 4.1.9

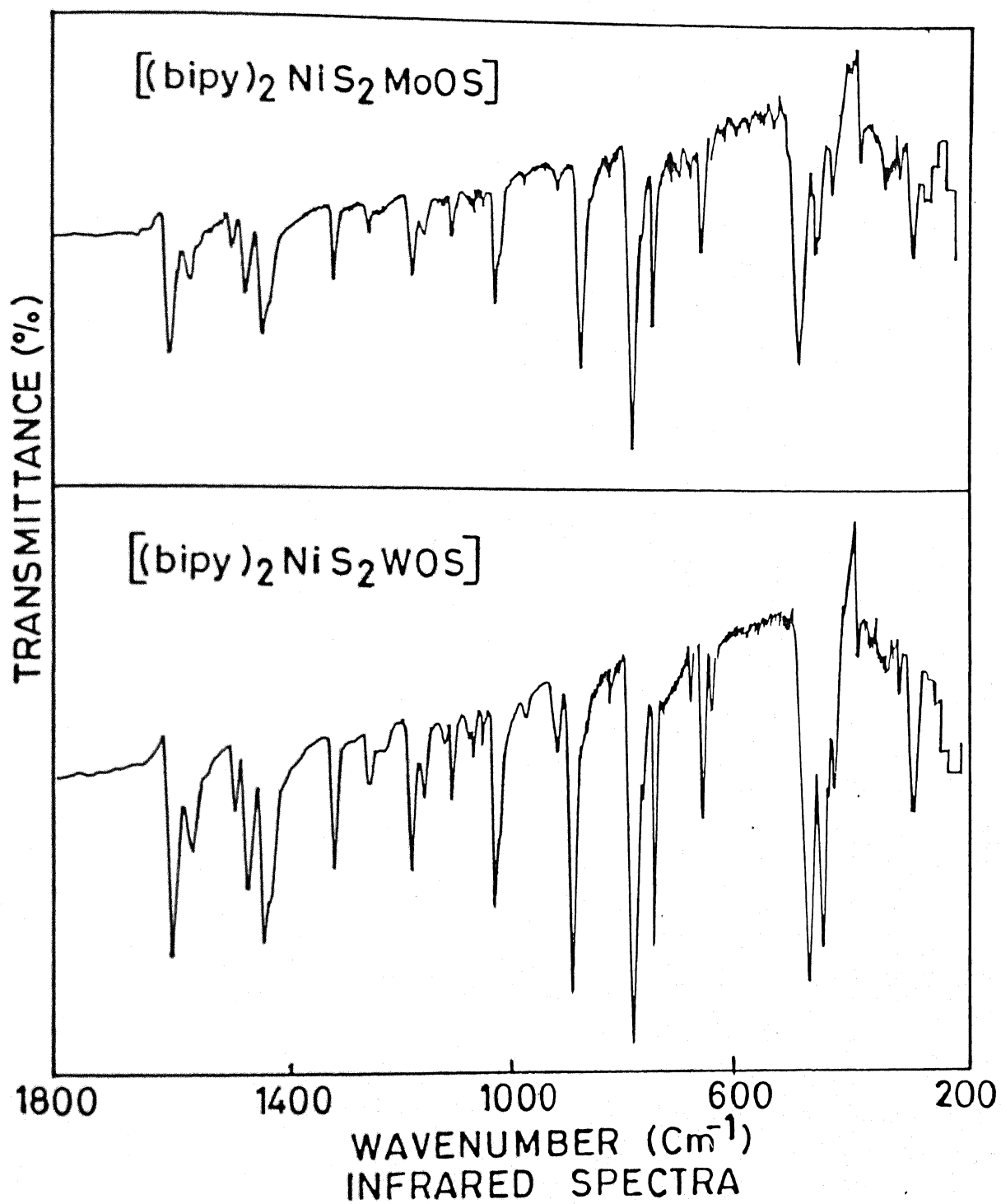


FIG. 4-1.10

$\nu(\text{MS}_{\text{br}})$ vibrations in the $400\text{--}500\text{ cm}^{-1}$ clearly indicates that the $[\text{MOS}_3]^{2-}$ ligands coordinate through the S ends and not via one sulfur and one oxygen. The IR spectra of all the oxotrithiometallato complexes are well in accord with the theoretical predictions. In the complexes having $[\text{WOS}_3]^{2-}$ ligands the terminal $\text{W}=\text{O}$ vibration appears at a higher frequency compared to the $\nu(\text{MoO})$ vibration in the analogous molybdenum complex. This observation suggests that there is stronger multiple bonding between tungsten and oxygen compared to molybdenum and oxygen. In fact, the terminal $\text{W}=\text{O}$ stretch always occurs at a higher frequency than $\nu(\text{MoO}_{\text{term}})$ in many compounds containing coordinated $[\text{MOS}_3]^{2-}$ ($\text{M}=\text{Mo}, \text{W}$) anions [12].

In all the complexes the aromatic diimines 2,2'-bipyridine and 1,10-phenanthroline have been used as coligands. These organic ligands are coordinated to the bivalent metal. The infrared spectra of complexes containing these ligands are well documented in the literature [142]. All the characteristic vibrations of these coordinated diimines are observed in all the complexes at around the same position. The infrared data for the coordinated diimines are listed in Table 4.2 .

4.2. Electronic spectroscopy:

The electronic spectra of the complexes were recorded on Cary-17D and Shimadzu UV-190 double beam spectrophotometers using matched quartz cells. For solid state spectra, the samples were prepared as KBr pellets.

The electronic spectra of the thiometallato complexes described in this work show characteristic absorption bands whose

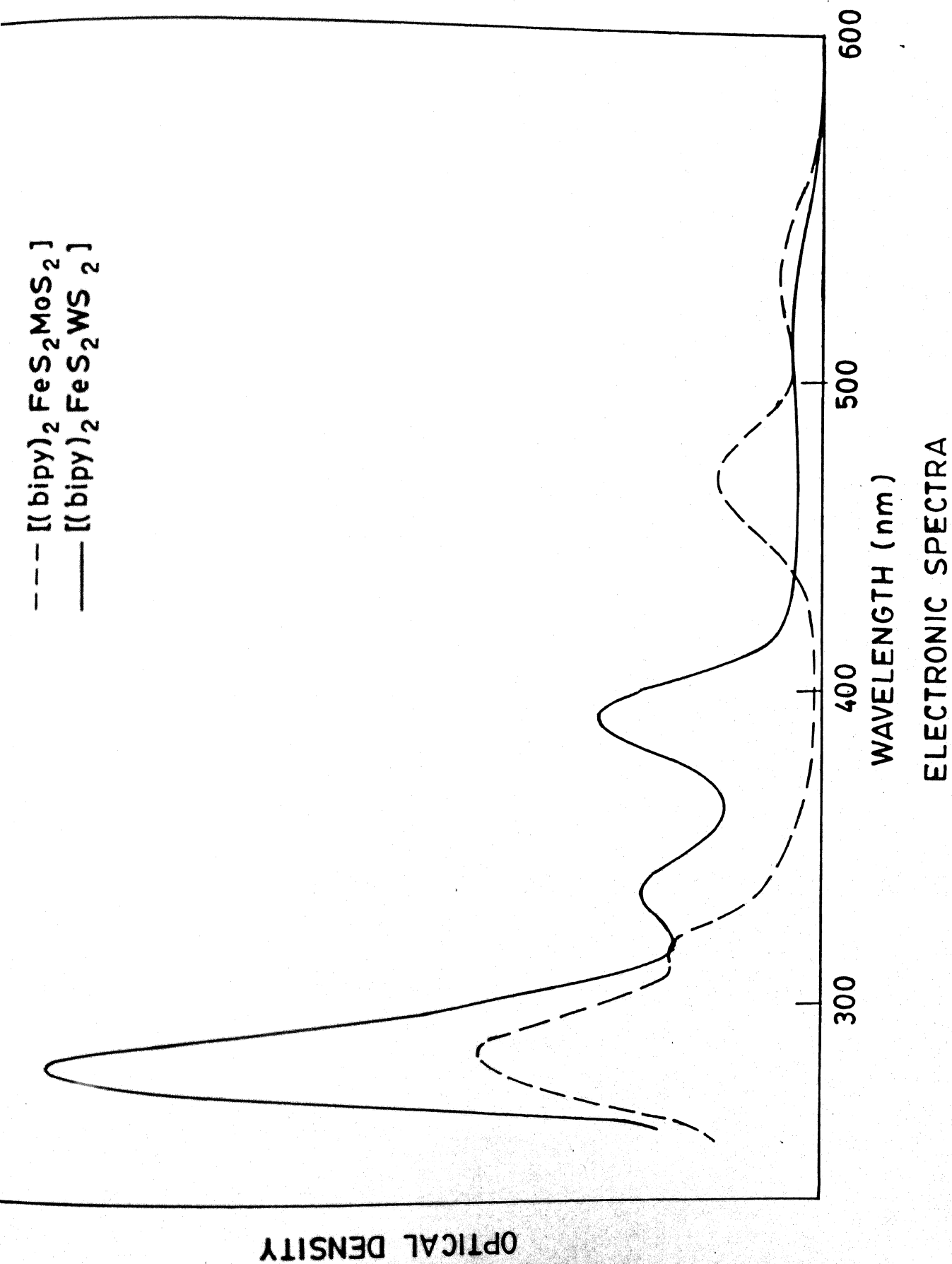
Table 4.2

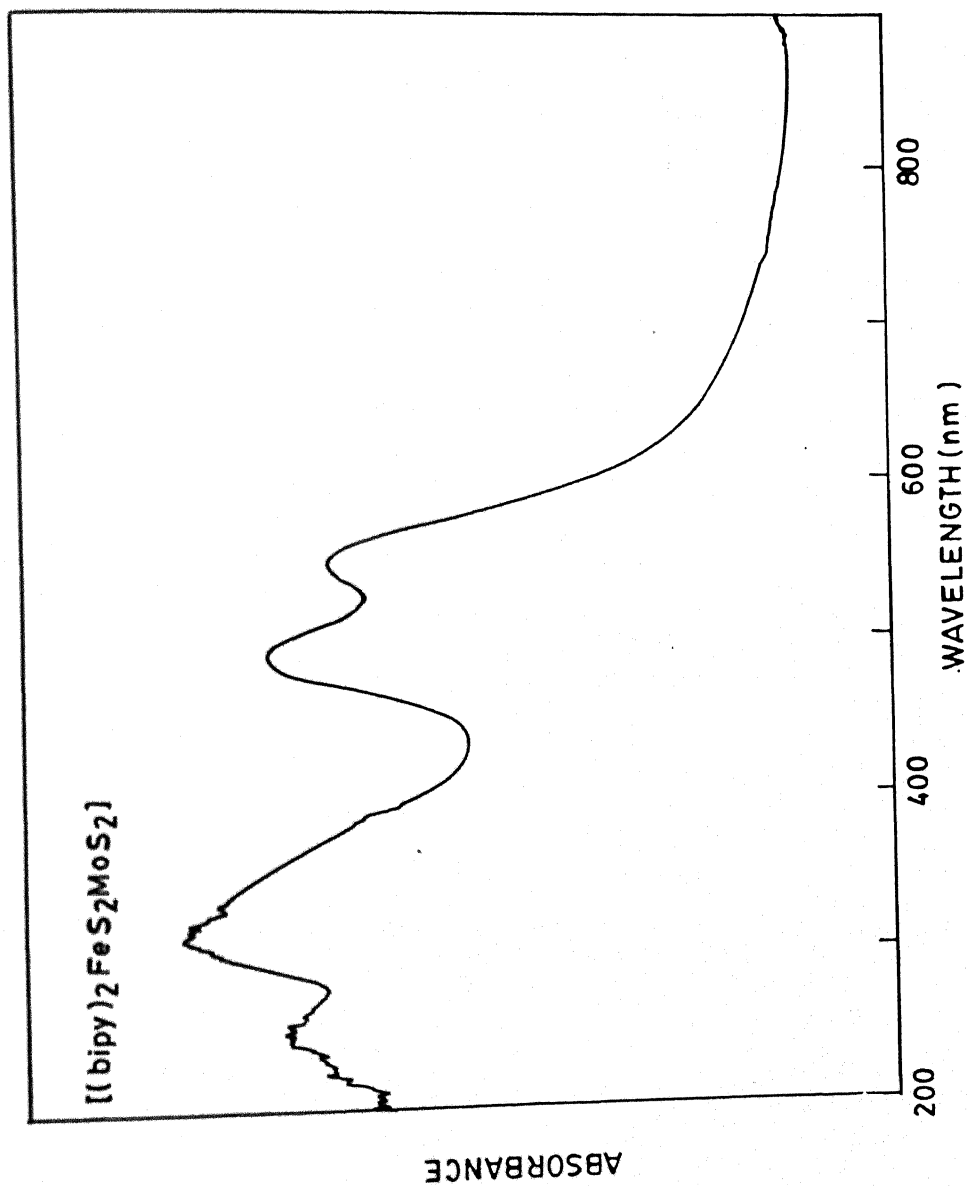
Infrared spectral data

Complex	Aromatic diimine vibrations (cm^{-1})
$[(\text{bipy})_2\text{MnS}_2\text{MoS}_2]$	775, 760, 735, 650, 630, 410, 350 ($\nu_{\text{Mn-S}}$) 235, 215 ($\nu_{\text{Mn-N}}$)
$[(\text{bipy})_2\text{MnS}_2\text{WS}_2]$	770, 760, 735, 650, 630, 410, 350 ($\nu_{\text{Mn-S}}$) 230, 210 ($\nu_{\text{Mn-N}}$)
$[(\text{bipy})_2\text{MnS}_2\text{MoOS}]$	770, 755, 735, 720, 630, 650, 410, 350 ($\nu_{\text{Mn-S}}$) 235 ($\nu_{\text{Mn-N}}$)
$[(\text{bipy})_2\text{MnS}_2\text{WOS}]$	975, 855, 775, 760, 735, 630, 650, 410
$[(\text{o-phen})_2\text{MnS}_2\text{MoS}_2]$	860, 840, 770, 720, 640, 410
$[(\text{o-phen})_2\text{MnS}_2\text{WS}_2]$	860, 845, 770, 720, 640
$[(\text{o-phen})_2\text{MnS}_2\text{MoOS}]$	970, 865, 850, 770, 725, 640
$[(\text{bipy})_2\text{FeS}_2\text{MoS}_2]$	1610, 1475, 1450, 1440, 1180, 910, 780, 760
$[(\text{bipy})_2\text{FeS}_2\text{WS}_2]$	1610, 1475, 1450, 1440, 1180, 910, 780, 750
$[(\text{bipy})_2\text{CoS}_2\text{MoS}_2]$	1610, 1480, 1450, 1320, 1190, 1040, 780, 750, 660
$[(\text{bipy})_2\text{NiS}_2\text{MoS}_2]$	1610, 1480, 1450, 1320, 1180, 1030, 780, 745, 650, 290 ($\nu_{\text{Ni-N}}$)
$[(\text{bipy})_2\text{NiS}_2\text{WS}_2]$	1610, 1480, 1450, 1320, 1180, 1035, 785, 750, 290 ($\nu_{\text{Ni-N}}$)
$[(\text{bipy})\text{NiS}_2\text{MoS}_2]$	1610, 1480, 1450, 1325, 1030, 770, 745, 660
$[(\text{bipy})\text{NiS}_2\text{WS}_2]$	1610, 1480, 1450, 1325, 1260, 1180, 1170, 770, 745, 660

positions are comparable to those in the free thiometallates. The ν_1 band arising from the S \rightarrow M charge transfer due to $t_1 \rightarrow 2e$ transition for the free tetrathiometallate is split due to the lowering of the symmetry in coordinated thiometallato complexes. In the present study, all the metal ions used in the syntheses of the complexes contain open d shell configuration. Thus, most of the d-d transitions which are weak in nature may lie under the envelope of the strong ligand to metal and metal to ligand charge transfer transitions. The nature of the splitting of the ν_1 band and other features of the electronic spectra of thiometallato complexes have been described earlier (Section 1.10.1).

The complexes synthesized in the present study, contain aromatic diimines as coligands. The electronic spectra of the complexes containing these ligands are very well documented in the literature [168]. It will be difficult to identify the ν_3 band of the coordinated thiometallate in these mixed ligand complexes as this transition appears in the same region where the intra-ligand charge transfer of 2,2'-bipyridine or 1,10-phenanthroline takes place. To observe weak d-d transitions a systematic variation of the thiometallato ligand ranging from $[\text{MoS}_4]^{2-}$, $[\text{MoOS}_3]^{2-}$, $[\text{WS}_4]^{2-}$ and $[\text{WOS}_3]^{2-}$ is helpful because in this fashion the positions of the strong characteristic absorption of the thiometallate ligand can be changed. The changing of the coligand from 2,2'-bipyridine to 1,10-phenanthroline can yield information about the ν_3 band of the coordinated thiometallate. The solution spectrum (Fig. 4.2.1) and the reflectance spectrum (Fig. 4.2.2) of the complex $[(\text{bipy})_2\text{FeMoS}_4]$ indicates that the compound retains its identity





DIFFUSE REFLECTANCE SPECTRUM
FIG. 4.2.2

in the polar solvent. The d-d bands in the electronic spectra of $[\text{Fe}(\text{diimine})_2\text{X}_2]$ complexes vary according to the different electronic ground states. Assuming approximate octahedral symmetry in $^5\text{T}_2$ ground state two bands of very weak intensity are observed in the NIR region. When the ground term is $^1\text{A}_1$ an absorption band arising from $^1\text{A}_1$ to $^3\text{T}_1$ may be observed around 960 nm which is also weak in nature [159]. For complexes with triplet ground state, a band of weak intensity around 830 nm is suggested. However, the assignment of this band is uncertain.

All the $[\text{Fe}(\text{diimine})_2\text{X}_2]$ complexes show a very intense charge transfer assigned to $\text{t}_{2\text{g}} \rightarrow \pi^*$ in the visible region, around 500-600 nm. It is interesting to note that this charge transfer transition takes place at almost exactly the same energy for both low spin and high spin complexes of this type. At energies higher than those of the charge transfer band internal π to π^* ligand transitions are observed. These transitions are usually shifted to lower energies compared to the free ligands. Uncoordinated $[\text{MoS}_4]^{2-}$ is also red in color and its lowest energy transition takes place at 467 nm. Thus for $[(\text{bipy})_2\text{FeMoS}_4]$ complex, the origin of the lowest energy absorption would be difficult to assign because of the reasons stated above. The absorption at 520 nm which is rather a broad one may thus be involved in several transitions. As the bidentate coordination of the $[\text{MoS}_4]^{2-}$ ligand will lower its symmetry from T_d to $\text{C}_{2\text{v}}$ on complexation, the splitting of ν_1 band is expected. The next band observed at 475 nm can be assigned to one of the components of the split ν_1 transition of the coordinated thiometallate.

The only complex, $[\text{Ni}(\text{en})_2\text{WS}_4]$ which falls under the category of the present series of complexes shows the splitting of ν_1 transition of the free $[\text{WS}_4]^{2-}$ on coordination at 429 and 523 nm in its reflectance spectrum [169]. However this complex is prepared from $[\text{Ni}(\text{en})_2\text{Cl}_2]$ which is dimeric in nature and thus it is difficult to say whether this Ni complex is monomeric or dimeric in nature. A point that is to be noted is that with hexacoordination around Ni and when $[\text{WS}_4]^{2-}$ is acting as a bidentate ligand the transitions arising due to the lowering of symmetry are red shifted. The next transition observed for $[(\text{bipy})_2\text{FeS}_2\text{MoS}_2]$ at 325 nm may be due to the ν_2 transition of the free $[\text{MoS}_4]^{2-}$ which remains unaltered as observed in earlier cases. According to MO calculation the ν_3 transition of free $[\text{MoS}_4]^{2-}$ should also be strongly disturbed on complexation. This transition is observed at 280 nm. However, the internal $\pi \rightarrow \pi^*$ of free 2,2'-bipyridine on complexation is usually shifted to lower energies. For free (bipy) this absorption appears around 280 nm and 235 nm respectively. The band contour of the 280 nm transition observed in the Fe complex is very much asymmetric in nature (Fig. 4.2.1) which suggests that this band is comprised of several transitions associated with $\pi \rightarrow \pi^*$ transition from the coordinated bipyridine.

The electronic spectrum of $[(\text{bipy})_2\text{FeS}_2\text{WS}_2]$ has a very broad band in the range 475-550 nm which can be resolved into two bands centered around 460 and 525 nm respectively. The origin of this band is due to $t_{2g} \rightarrow \pi^*$ transition originating from $\{(\text{bipy})_2\text{Fe}\}$ moiety. This shows that the band at 475 nm, is one of the

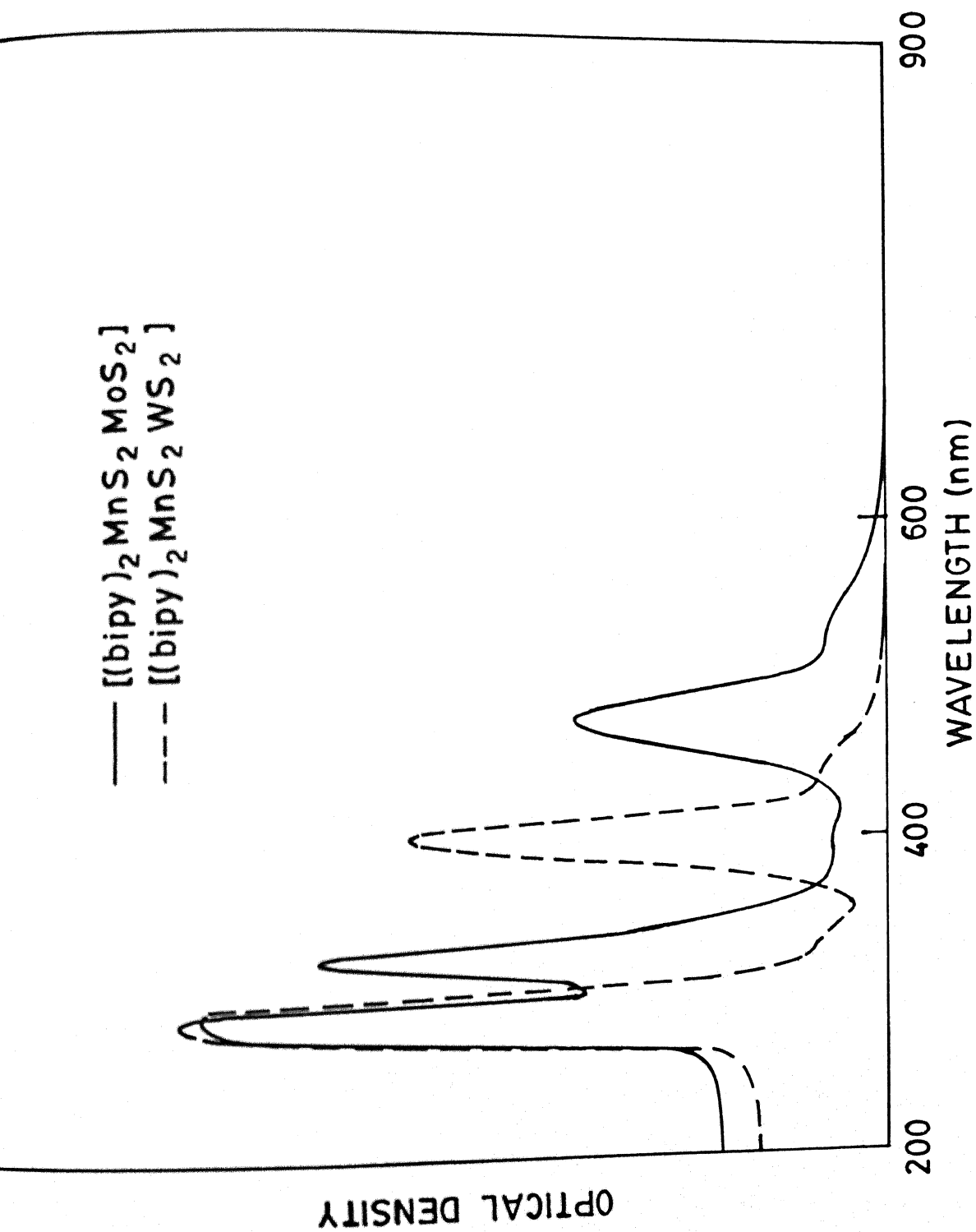
components of the ν_1 band of free $[\text{WS}_4]^{2-}$ when it is coordinated in bidentate fashion. The other component of this band is observed at 393 nm which remains almost unaltered from the position of free $[\text{WS}_4]^{2-}$. The reason for the appearance of this absorption in same energy is not clear. The highest energy absorption band for this complex appears at 280 nm. This band can be assigned to $\pi \rightarrow \pi^*$ transition of the coordinated diimine. Similar arguments can also be extended for the other complexes. The electronic spectral data are listed in Table 4.3 .

The identification of the ν_1 band of $[\text{MS}_4]^{2-}$ (M= Mo,W) when coordinated to $\{\text{Fe}(\text{bipy})_2\}$ core causes problem because the charge transfer transition from bipyridine to iron center appears around the same energy. This problem can be effectively sorted out when the thiometallates are coordinated to bipyridine complexes of Mn,Co,Ni. The electronic spectra of the Mn-thiometallate complexes are presented in Fig. 4.2.3 and the diffuse reflectance spectra of $[(\text{bipy})_2\text{NiMS}_4]$ is presented in Fig. 4.2.4 . In the thiometallate complexes of these metals the charge transfer between bipyridine and these metal centers in the near ultraviolet region. In the case of Mn(II) the forbidden d-d transitions should not disturb the positions of the split ν_1 transitions. Thus for all these complexes the two transitions around 520 and 470 nm regions could be assigned due to the splitting of the transitions for the lowering of the symmetry of coordinated thiometallate. The pattern is observed for the coordinated thiotungstate complexes. The spectral data are summarized in Table 4.3 .

Table 4.3

Electronic spectral data of the synthesized complexes

Complex	Band maxima (nm)
$(\text{NH}_4)_2\text{MoS}_4$	463, 316, 240
$[(\text{bipy})_2\text{MnS}_2\text{MoS}_2]$	520, 475, 325, 280
$[(\text{bipy})_2\text{MnS}_2\text{WS}_2]$	430(sh), 400, 280
$[(\text{bipy})_2\text{MnS}_2\text{MoOS}]$	480, 405, 325, 285
$[(\text{bipy})_2\text{MnS}_2\text{WOS}]$	420(sh), 400, 340, 280
$[(\text{o-phen})_2\text{MnS}_2\text{MoS}_2]$	530, 475, 320, 293
$[(\text{o-phen})_2\text{MnS}_2\text{WS}_2]$	425, 400, 280
$[(\text{bipy})_2\text{FeS}_2\text{MoS}_2]$	530, 470, 320, 285
$[(\text{bipy})_2\text{FeS}_2\text{WS}_2]$	525, 391, 335, 280
$[(\text{bipy})_2\text{FeS}_2\text{MoOS}]$	525, 475, 393, 285
$[(\text{bipy})_2\text{FeS}_2\text{WOS}]$	335, 280
$[(\text{bipy})_2\text{CoS}_2\text{MoS}_2]$	525(sh), 475, 320, 285
$[(\text{bipy})_2\text{CoS}_2\text{WS}_2]$	420(sh), 395, 280
$[(\text{bipy})_2\text{NiS}_2\text{MoS}_2]$	498, 316, 260
$[(\text{bipy})_2\text{NiS}_2\text{WS}_2]$	460(sh), 415, 304, 260
$[(\text{o-phen})_2\text{NiS}_2\text{MoS}_2]$	495, 310, 280
$[(\text{o-phen})_2\text{NiS}_2\text{WS}_2]$	410, 280
$[(\text{bipy})\text{NiS}_2\text{MoS}_2]$	515, 400(sh), 330, 295
$[(\text{bipy})\text{NiS}_2\text{WS}_2]$	430, 390, 295
$[(\text{bipy})\text{NiS}_2\text{MoOS}]$	465, 390, 310
$[(\text{bipy})\text{NiS}_2\text{WOS}]$	430, 375, 290



ELECTRONIC SPECTRA

FIG. 4.2.3

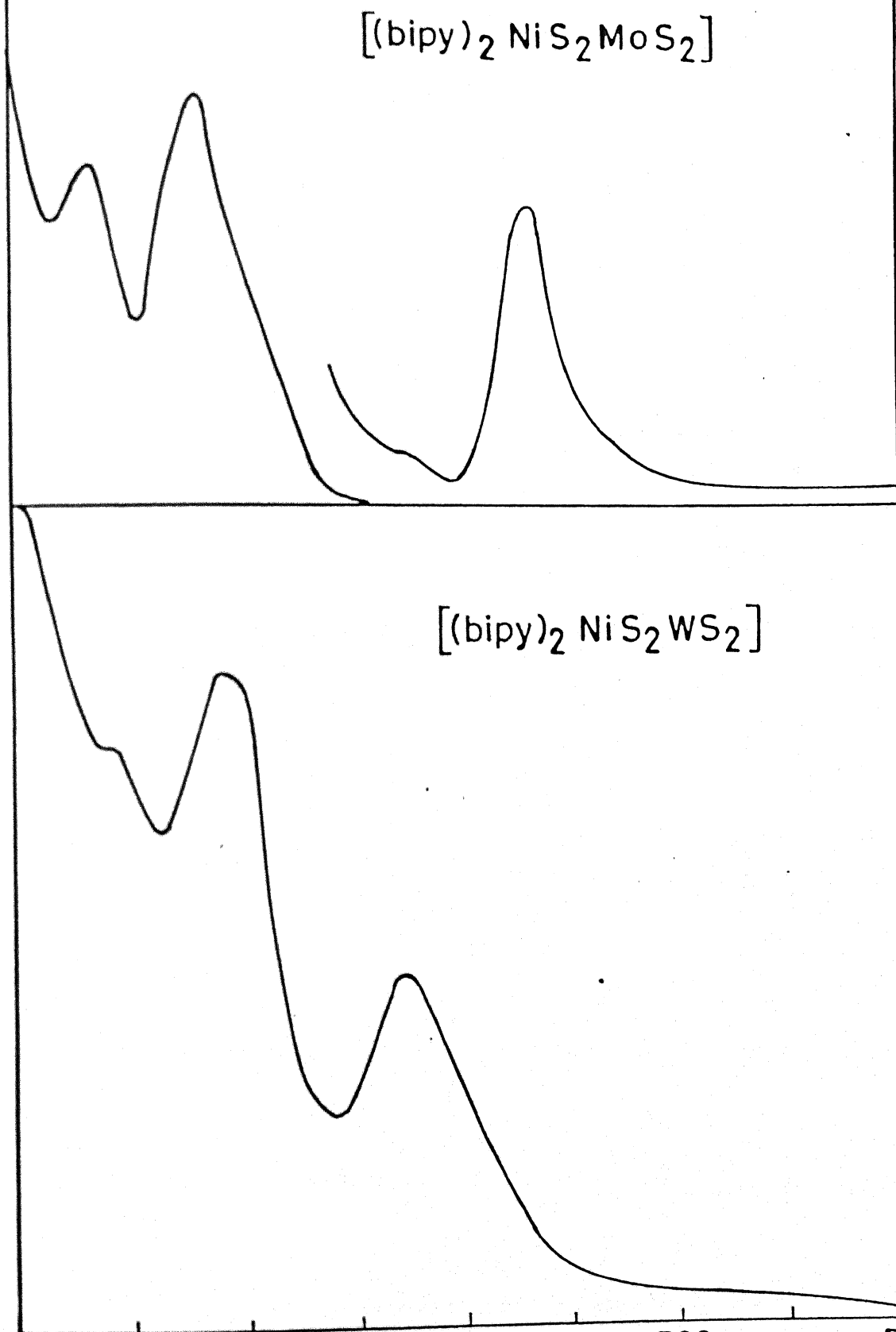


ABSORBANCE

220 340 460 580 700
WAVELENGTH (nm)

DIFFUSE REFLECTANCE SPECTRA

FIG. 4.2.4



4.3 Magnetic susceptibility measurements:

The room temperature magnetic susceptibility data of the Mn, Co, and Ni thiometallate complexes were recorded by Prof. T.R. Rao at the Banaras Hindu University, Varanasi using a Cahn-Faraday magnetic balance. $[\text{CoHg}(\text{SCN})_4]$ was used as the calibrant. The data were collected at an applied field of 10,000 gauss. The magnetic susceptibility measurements of the iron-thiometallate complexes were recorded by Prof. S. Mitra at Tata Institute of Fundamental Research, Bombay on an automatic Oxford Faraday Instrument.

The magnetic susceptibility data of the synthesized complexes may provide an understanding of the relative strength of the thiometallate ligands as the magnetic properties of complexes are a manifestation of the ligand field strength [170]. The magnetic properties of the thiometallato complexes are summarized in Table 4.4. As expected the salts $[\text{FeL}_3]\text{MoS}_4$, (M=Mo,W; L=o-phen) are diamagnetic. The magnetic behavior of a series of bis(diimine) complexes of Fe(II) of the type $[\text{FeL}_2\text{X}_2]$ (L=bipy or o-phen; $\text{X}=\text{Cl}^-$, NCS^- , Cl^- , Br^- , I^- , N_3^- , HCOO^- , etc.) have been extensively studied by König and coworkers [159,171-173]. It has been observed that when $\text{X}=\text{CN}$ the complexes are diamagnetic, and when $\text{X}=\text{Cl}, \text{Br}, \text{I}$ etc. the complexes are high spin. The bis(diimine) complexes $[\text{FeL}_2\text{X}_2]$ where $\text{X}=\text{SCN}^-$ exhibit complicated temperature dependence of the magnetic moment and ground states of intermediate spin ($S=1$) are encountered within the series $[\text{FeL}_2\text{X}_2]$ where X_2 stands for bidentate oxalate or malonate.

Table 4.4

Room temperature magnetic susceptibility data for
the synthesized complexes

Complex	$\chi_M \times 10^6$	μ_{eff} BM
o-phen) ₃ MoS ₄	---	Diamagnetic
o-phen) ₃ WS ₄	---	Diamagnetic
ipy) ₂ FeS ₂ MoS ₂ l	1034	1.884*
ipy) ₂ FeS ₂ WS ₂ l	1828	2.72*
ipy) ₂ FeS ₂ MoOSl	---	Diamagnetic
ipy) ₂ FeS ₂ WOSl	---	Diamagnetic
ipy) ₂ CoS ₂ MoS ₂ l	3407	2.88
ipy) ₂ CoS ₂ WS ₂ l	4312	3.24
ipy) ₂ NiS ₂ MoS ₂ l	924	1.50
ipy) ₂ NiS ₂ WS ₂ l	1768	2.08
-phen) ₂ NiS ₂ MoS ₂ l	1750	2.07
ipy) ₂ MnS ₂ MoS ₂ l	6358	3.94
ipy) ₂ MnS ₂ WS ₂ l	10060	4.94
ipy) ₂ MnS ₂ MoOSl	5904	3.88
ipy) ₂ MnS ₂ WOSl	8909	4.74
phen) ₂ MnS ₂ MoS ₂ l	7266	4.3
phen) ₂ MnS ₂ WS ₂ l	10303	5.02
phen) ₂ MnS ₂ MoOSl	4997	3.6
py)NiS ₂ MoS ₂ l	---	Diamagnetic
py)NiS ₂ WS ₂ l	---	Diamagnetic
phen)NiS ₂ MoS ₂ l	---	Diamagnetic

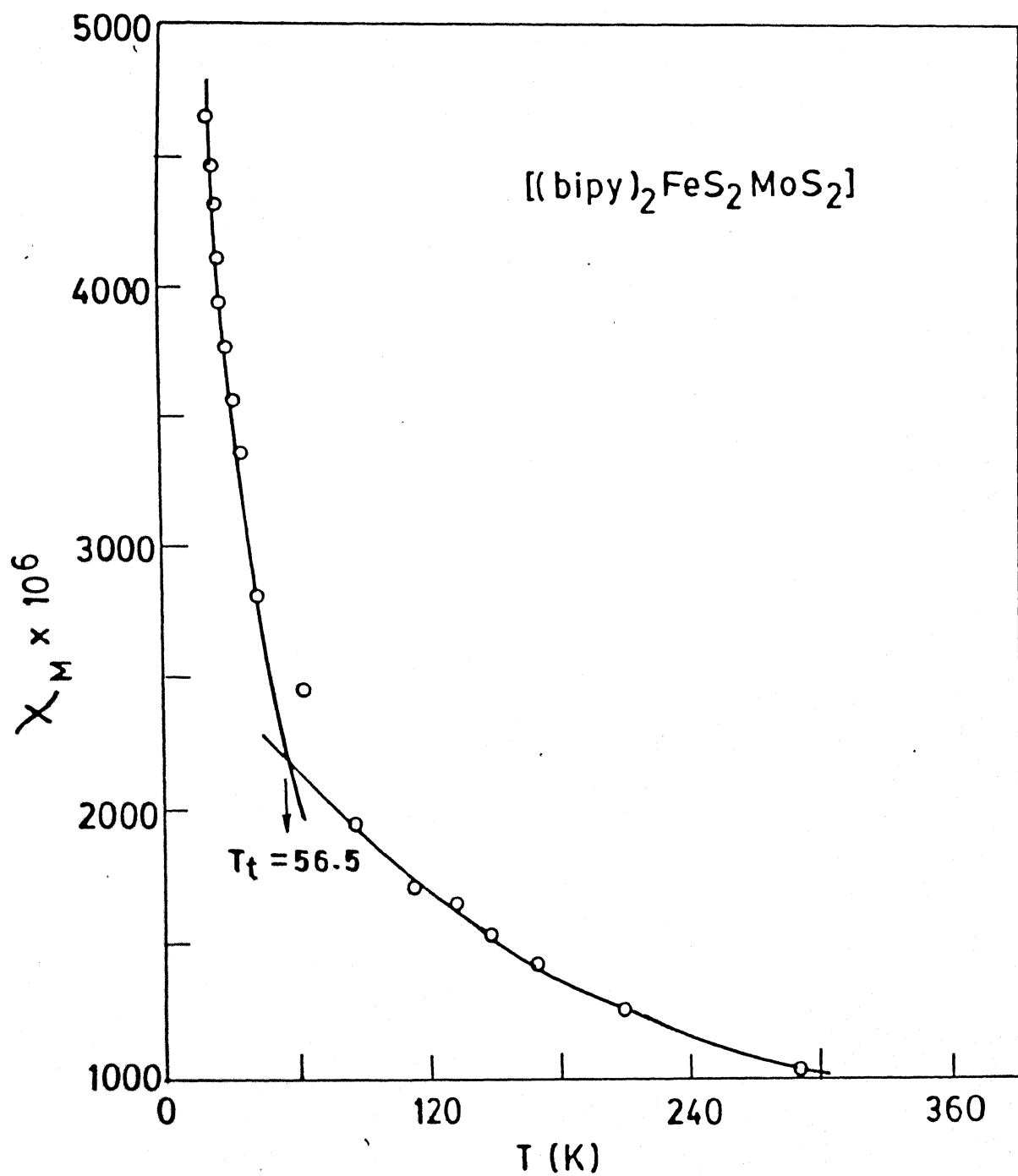
* μ_{eff} values from Curie-Weiss plot

The bis(diimine)iron(II) complexes $[\text{Fe}(\text{bipy})_2\text{X}_2]$ synthesized by us show interesting magnetic properties. The complexes where $\text{X}_2 = [\text{MOS}_3]$ ($\text{M} = \text{Mo}, \text{W}$) are diamagnetic in nature and the complexes where $\text{X}_2 = [\text{MS}_4]$ have an effective magnetic moment which is far below the expected value for four unpaired electrons for a high-spin $\text{Fe}(\text{II})$. The magnetic behavior of the complexes $[(\text{bipy})_2\text{FeMS}_4]$ ($\text{M} = \text{Mo}, \text{W}$) have been studied at various temperatures and the data are presented in Table 4.5. Both the complexes obey the Curie-Weiss law in the temperature range 60-291 K. The χ vs T and $1/\chi$ vs T plots for these complexes are presented in Figs. 4.3.1 to 4.3.4. From Figs. 4.3.1 and 4.3.3 it is very clear that there is a transition temperature ($T_t = 56.6$ K for the Mo complex and $T_t = 59.8$ K for the W Complex) below which the complexes can possibly have a ferromagnetic behavior. This low temperature region has not been examined in detail. The same observations can also be obtained from the $1/\chi$ vs T plot. In the $1/\chi$ vs T plot (Figs 4.3.2 and 4.3.4) the broken line indicates the least square plot taking into account all the experimental points in the entire temperature range (291 K - 20 K). From the plot it is clear that such a line does not fit all the points well. Hence, the experimental points below 45 K have been fitted separately and all the other points above this temperature have been fitted as another line. Now it can be inferred from the $1/\chi$ vs T plots that the separate fittings are very good in both the regions. The point of intersection of these two lines can be identified as the transition temperature (T_t) which is the same as obtained from the χ vs T plot.

Table 4.5

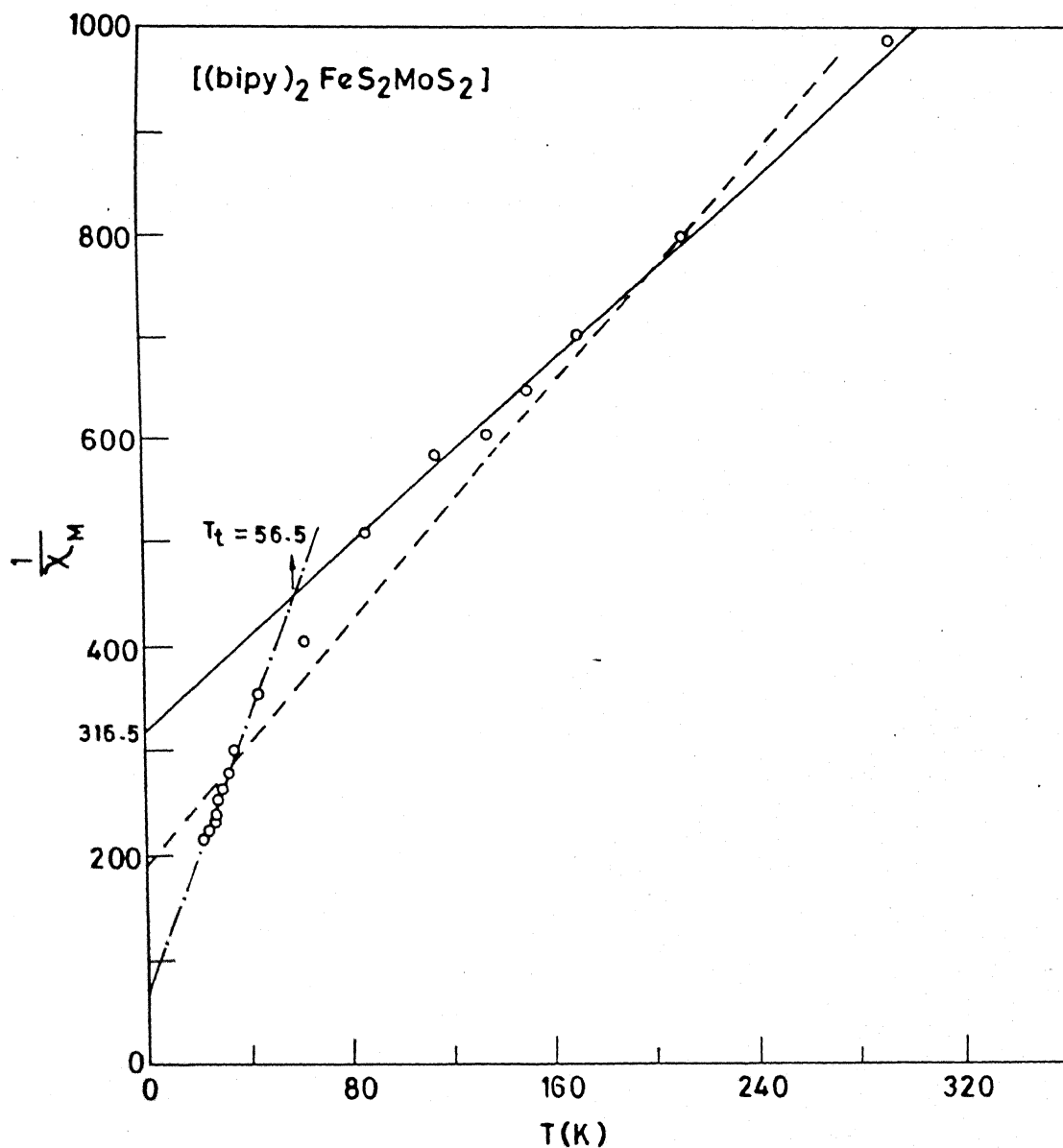
Magnetic susceptibility data of $[(bipy)_2FeS_2MS_2]$

$(bipy)_2FeS_2MoS_2$		$(bipy)_2FeS_2WS_2$	
Temp. K	$\chi'_M \times 10^6$	Temp. K	$\chi'_M \times 10^6$
22.3	4651.3	20.00	6592.11
23.7	4441.05	22.65	5991.24
25.15	4314.84	25.01	5690.81
26.54	4104.5	26.72	5390.37
28.02	3936.3	28.17	5175.78
29.80	3768.05	29.77	5004.09
31.90	3557.75	32.26	4617.84
35.15	3347.45	35.34	4489.09
43.50	2800.65	43.64	4317.39
62.50	2464.16	61.00	3416.09
85.91	1959.40	82.27	3072.74
114.50	1707.07	103.82	2815.22
133.50	1665.00	124.09	2643.54
150.87	1538.82	151.30	2471.87
171.74	1412.64	170.50	2343.12
210.00	1244.40	205.00	2257.27
291.00	1034.09	291.00	1828.08



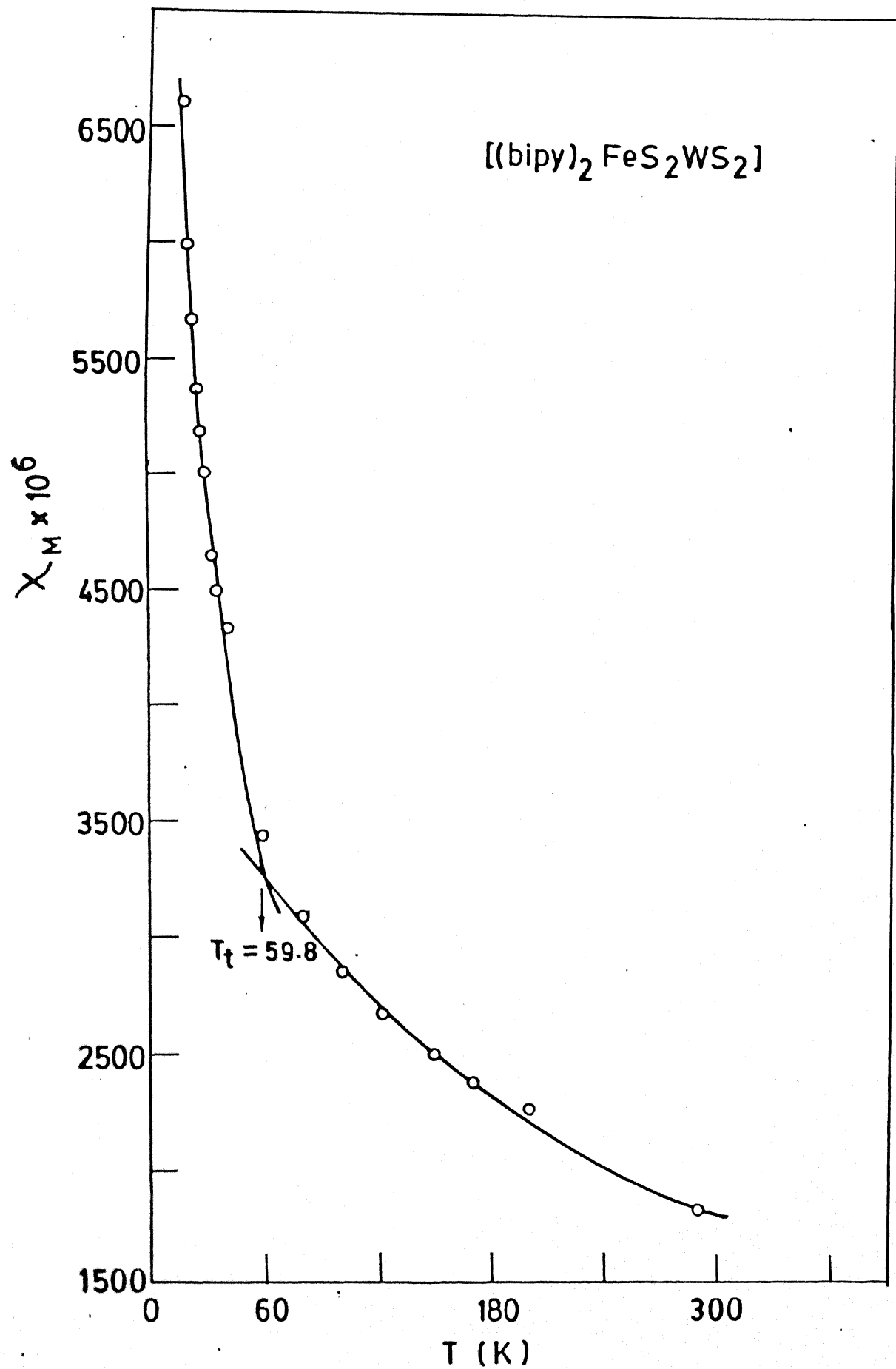
SUSCEPTIBILITY VS. TEMPERATURE

FIG. 4-3.1

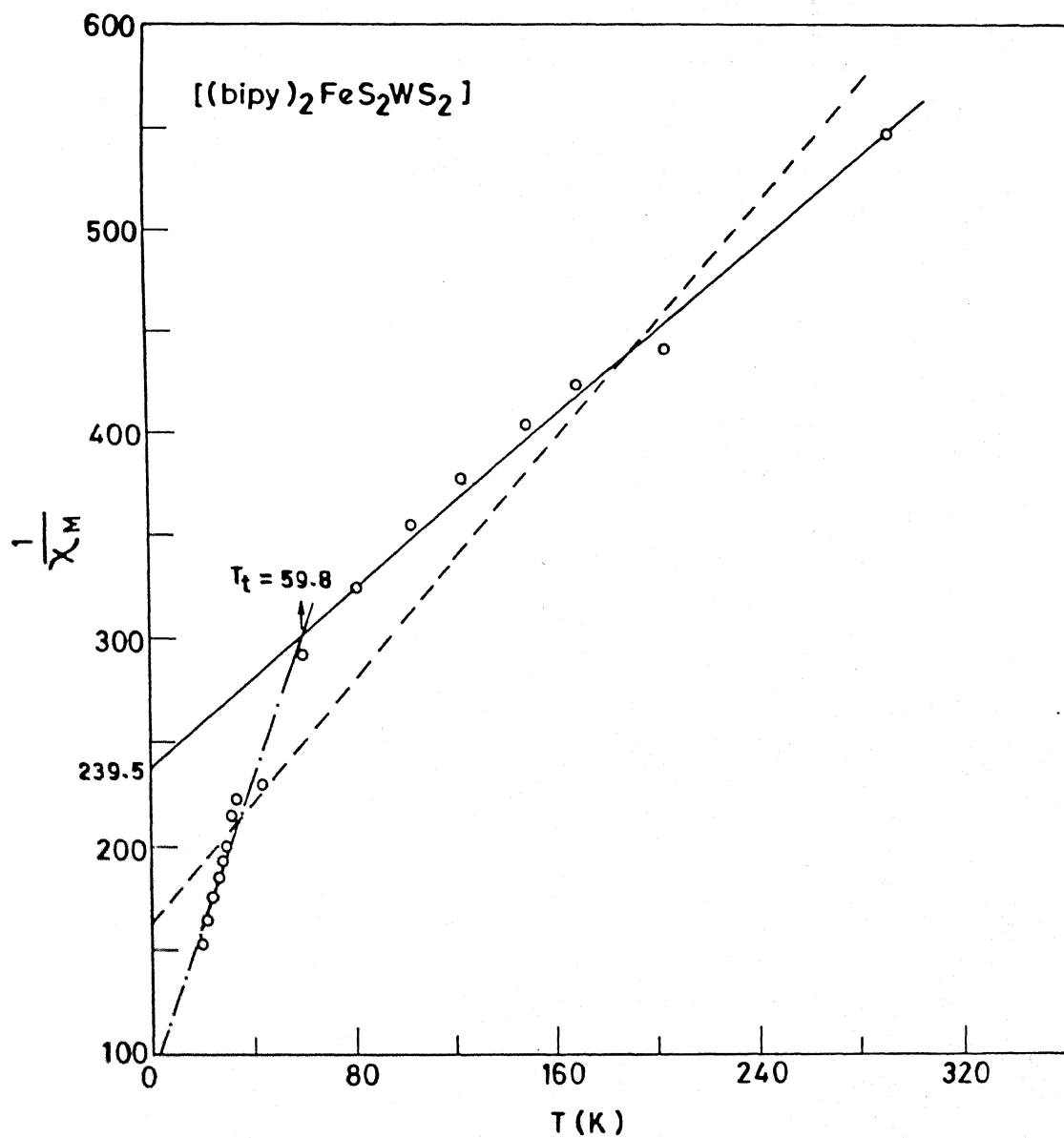


RECIPROCAL SUSCEPTIBILITY VS. TEMPERATURE

FIG. 4.3.2



SUSCEPTIBILITY VS TEMPERATURE



RECIPROCAL SUSCEPTIBILITY VS. TEMPERATURE

FIG. 4-3-4

Both the complexes obey the Curie-Weiss law above the transition temperature. The μ_{eff} calculated from the slope of the line turns out to be 1.89 BM for $[(\text{bipy})_2\text{FeS}_2\text{MoS}_2]$ and 2.72 BM for $[(\text{bipy})_2\text{FeS}_2\text{WS}_2]$ which is less than the expected value for high spin Fe(II). It is interesting to note that the corresponding oxotrithiometallates are diamagnetic. It can be inferred from this that the oxotrithiometallates are stronger ligands as compared to their tetrathio counterparts. The low values of the effective magnetic moment of the tetrathiometalato complexes can arise as a consequence of one of the following:

- i) Admixture of low-spin Fe(III) complex with high-spin Fe(II) complex.
- ii) Ferromagnetic impurity in low spin Fe(II) complex.
- iii) Antiferromagnetic interaction in high spin Fe(II) complex or Fe(I) complex.

The possibility of an admixture of Fe(III) complex seems very unlikely due to the fact, that thiometallate anions are sufficiently reducing in nature to cause the reduction of ferric iron to ferrous iron and $[\text{MoS}_4]^{2-}$ is known to reduce Fe(II) to Fe(I) in the formation of the trinuclear complex $[\text{Fe}(\text{MoS}_4)_2]^{3-}$ [101-104]. The formation of Fe(I) can be ruled out from the analytical and infrared data. The presence of a ferromagnetic impurity in low spin Fe(II) complex can also be ruled out from the fact that the oxotrithiometallate complexes are diamagnetic. Since the synthetic procedure for all the complexes is the same, if an impurity is present it should be there in all the systems and it is very unlikely that this impurity should remain absent

in the $[(bipy)_2FeS_2MOS]$ complexes. The fact that two of the complexes behave differently rules out the presence of any impurity. It is well known that in the absence of aromatic diimines the reaction between iron salts and $[MoS_4]^{2-}$ result in the formation of FeS and MoS_3 [155]. If it is assumed that the peculiar magnetic behavior is due to the presence of such antiferromagnetic impurities, this can also be ruled out from the shape of the χ vs T plot, where χ decreases with increase in temperature below the transition temperature. The transition temperatures for both the complexes are fairly close whereas the Weiss constant θ varies too much from -140.4 K for the Mo complex to -226.5 K for the W complex. The high negative values of θ suggests that there exists an antiferromagnetic interaction in the region above the transition temperature where the complexes obey Curie-Weiss law. This may probably be the reason for the low values of the observed magnetic moments of the complexes. It is important to note here that all the complexes are isostructural as shown by their X-ray powder pattern (vide infra). A solution magnetic study by Evans method [174] should have thrown some light to resolve most of these ambiguities but the restricted solubility of the complexes in common solvents prevented such a study. The paucity of data, makes it impossible to get a clearer picture of these magnetic interactions, nevertheless the observation that the oxotrithiometallato complexes are diamagnetic is indicative of the fact that the oxotrithiometallates are stronger ligands as compared to the tetrathiomallates.

The χ_M values of the corresponding Co and Ni thiometallate complexes have been measured at room temperature and the μ_{eff} values have been calculated using the formula $\mu_{\text{eff}} = 2.84\sqrt{\chi_M \times T}$. The effective magnetic moments thus calculated are less than the expected values for 3 and 2 unpaired electrons, respectively (Table 4.4). Co(II) complexes of the type $[\text{Co}(\text{terpy})_2]^{2+}$ (terpy=terpyridyl) with reduced magnetic moments have been shown to exhibit complicated magnetic behavior [175]. All the Fe, Co and Ni complexes are isostructural. It is very likely that in these complexes also there can be such antiferromagnetic interactions as in the Fe case which causes the quenching of the spin. An interesting observation is that the μ_{eff} values for the thiomolybdate series is less as compared to the thiotungstate series.

The μ_{eff} values of the Mn-thiometallato complexes are also listed in Table 4.4. For Mn(II) if we assume that the ligand field strength of the thiometallate ligand does not exceed that of the aromatic diimines a high-spin configuration is expected. However, the observed magnetic moments are less than that expected for 5 unpaired electrons. The exact reason for the slight reduction in the μ_{eff} values is not clearly understood. However, the EPR studies of the Mn complexes show Mn(II) to be high spin d^5 system (Section 4.4.2). A notable trend can be observed in the μ_{eff} values. The μ_{eff} values for the Mo complexes are less than that of the corresponding W complexes. The μ_{eff} values of the oxotrithiometallates are less than that of the tetrathiometallates. If the reduction in the magnetic

moments can be attributed due to some sort of spin-exchange interactions, then such interactions are stronger in the Mn-Mo complexes as compared to the Mn-W complexes. The tetracoordinated Ni-thiometallate complexes are diamagnetic in nature and hence a distorted square planar arrangement can be anticipated for these complexes with a planar $\{N_2NiS_2\}$ moiety. Due to the lack of structural data and temperature dependent magnetic data, for the Mn, Co, and Ni thiometallate complexes no further arguments can be extended. A thorough study of the magnetic properties is under way.

4.4 Magnetic resonance studies:

The compounds synthesized in this study have the general formula $[L_2M'(MS_4)]$ where (L=o-phen, bipy; $M'=Mn, Fe, Co, Ni$; $M=Mo, W$). The magnetic properties of the open d-shell M' ions can give rise to interesting structural features. The solubility restrictions of the complexes precluded the evaluation of the magnetic data by NMR method [174]. So, the EPR spectra of the complexes were recorded and the results are discussed below.

The complexes with $M'=Fe, Co, Ni$ do not show any room temperature EPR signals. However, when $M'=Mn$ a broad isotropic spectrum has been observed for which dilution studies were undertaken both in solid and solution phases and the results are explained in Section 4.4.2. Considering the strong spin-orbit coupling and low lying orbital energy levels of Fe(II) and Co(II) in a crystalline environment, a small value of spin lattice relaxation time (T_1) and consequently undetectably broad room

temperature spectra for such species is expected [176]. However, the resonance can be detected at very low temperatures and we have observed such spectra for the complexes $[(bipy)_2FeMS_4]$ and the results are discussed in Section 4.4.3.

4.4.1 Experimental

The EPR spectra were recorded using a Varian E-109 spectrometer operating at X-band. DPPH was used as a frequency calibrant. A microwave power of ~ 2 mW was used for all the spectra. The spectra of all the complexes were recorded at room temperature except for the iron-thiometallate complexes for which low temperature (6-34 K) EPR spectral measurements were done at the University of Massachusetts, Boston, by Prof. Hans van Willigen. All the EPR absorptions have been shown in the first derivative form, and the field marking is indicative of DPPH resonance positions.

4.4.2 EPR spectra of Mn-thiometallate complexes;

Mn(II) is d^5 system and in the hexacoordinate complexes $[L_2MnMS_4]$ is of high-spin nature. The ground state is an orbital singlet $^6S_{5/2}$ which to first order should not interact with the crystalline electric field. However, to higher order the combined action of an electric field gradient and the spin-spin interaction does split the energy levels. The magnitude of this Zero field splitting is expressed by the axial field splitting parameter, D for the case of an axial distortion. The spin Hamiltonian is given by,

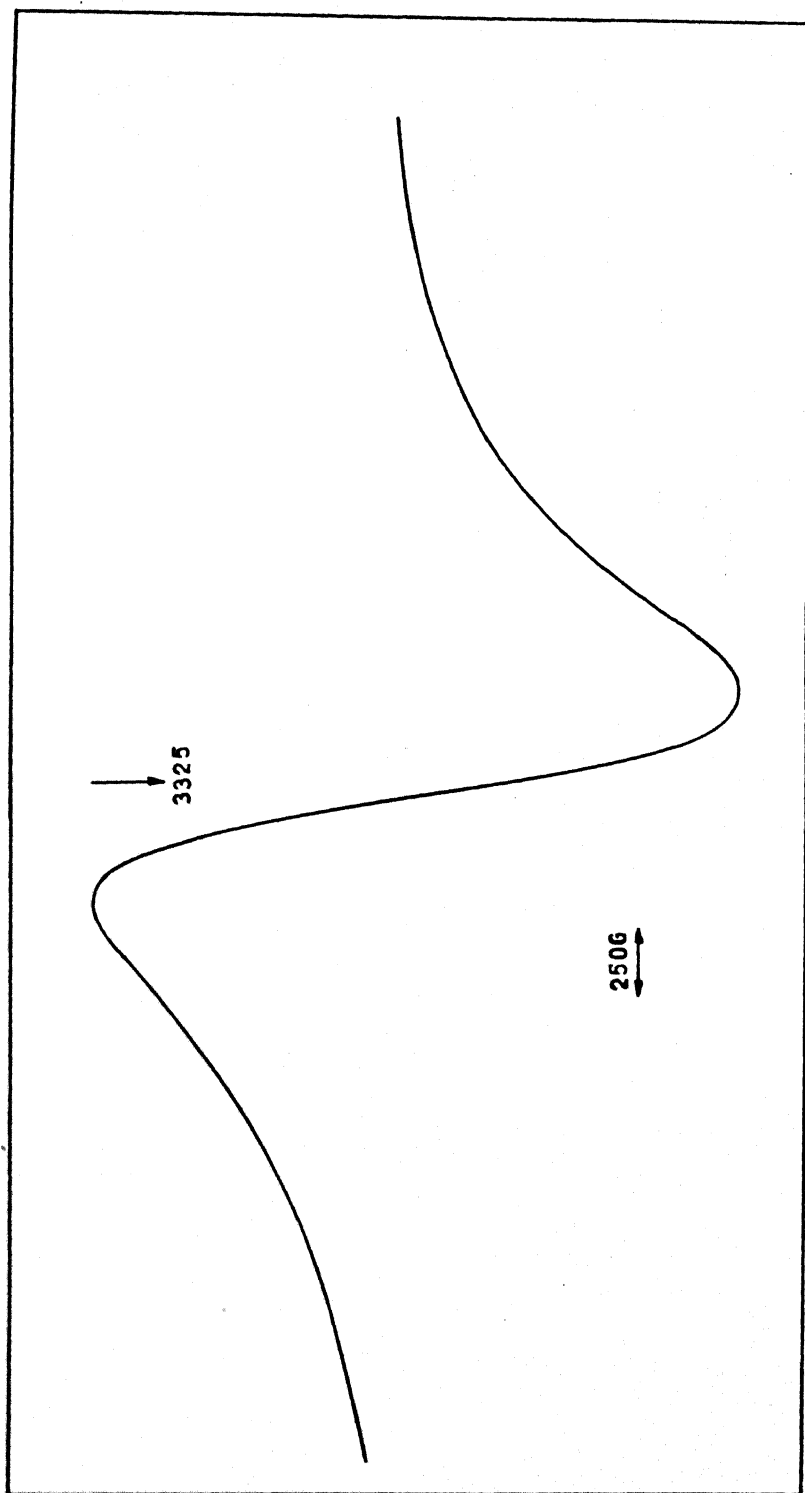
$$\mathcal{H} = g\beta \mathbf{H} \cdot \mathbf{S} + D[S_z^2 - 1/3 S(S+1)] + A \cdot \mathbf{S} \cdot \mathbf{I}$$

where \mathbf{H} is the magnetic field vector, g is the spectroscopic splitting factor, β is the Bohr magneton, A is the Mn hyperfine splitting constant, \mathbf{S} is the electronic spin vector, \mathbf{I} is the nuclear spin vector, $S = 5/2$ and S_z is the diagonal spin operator. Neglecting the nuclear hyperfine splittings, five transitions corresponding to $\Delta M_S = \pm 1$ would be expected in an oriented single crystal since M_S can have the values $\pm 5/2$, $\pm 3/2$ and $\pm 1/2$. The transitions are

$$\begin{aligned} \pm 5/2 &\longleftrightarrow \pm 3/2 & h\nu &= g\beta H \pm 2D(2\cos^2\theta - 1) \\ \pm 3/2 &\longleftrightarrow \pm 1/2 & h\nu &= g\beta H \pm D(3\cos^2\theta - 1) \\ + 1/2 &\longleftrightarrow - 1/2 & h\nu &= g\beta H \end{aligned}$$

where θ is the angle between the applied magnetic field and the direction of the axial distortion. In a polycrystalline specimen, only the $+1/2 \longleftrightarrow -1/2$ transition is observed since the angular dependence of the $\pm 5/2 \longleftrightarrow \pm 3/2$ and $\pm 3/2 \longleftrightarrow \pm 1/2$ transitions broadens these peaks beyond resolution. For Mn(II) each of these lines is further split into a sextet by the nuclear hyperfine interaction of ^{55}Mn ($I=5/2$, abundance 100 %). This may be explained as arising due to the core polarization of 2s and 3s electrons by the net spin of 3d electrons [177].

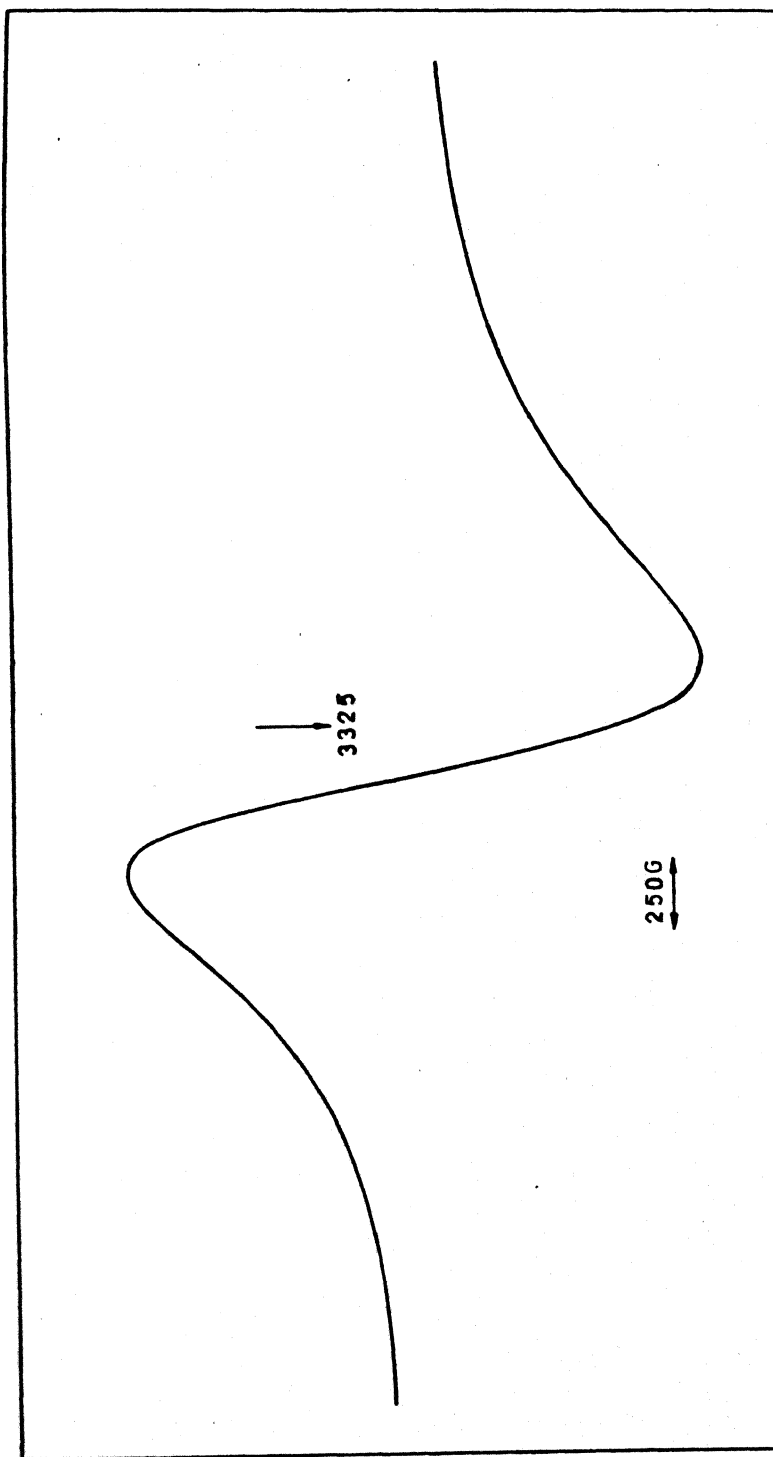
The powder EPR spectra of some Mn-thiometallate complexes are depicted in Figs. 4.4.1 to 4.4.4. These spectra show a broad isotropic signal around $g \approx 2.0011$. The broadness of the spectra is due to spin-exchange interactions and dipolar interactions.



Magnetic field (G)

EPR SPECTRUM OF POLYCRYSTALLINE $[(\text{bipy})_2 \text{MnS}_2\text{MoS}_2]$

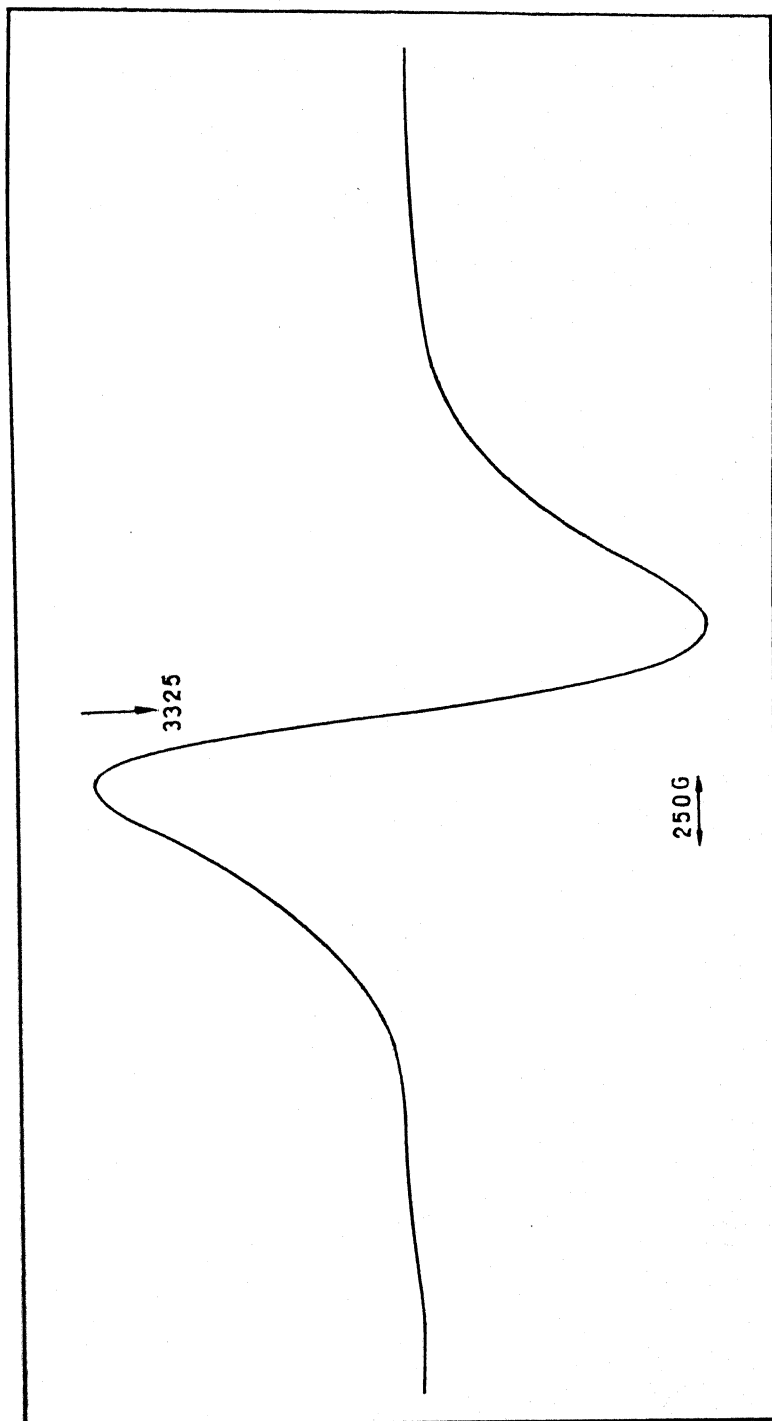
FIG. 4.4.1



Magnetic field (G)

EPR SPECTRUM OF POLYCRYSTALLINE $[(\text{bipy})_2 \text{MnS}_2\text{WS}_2]$

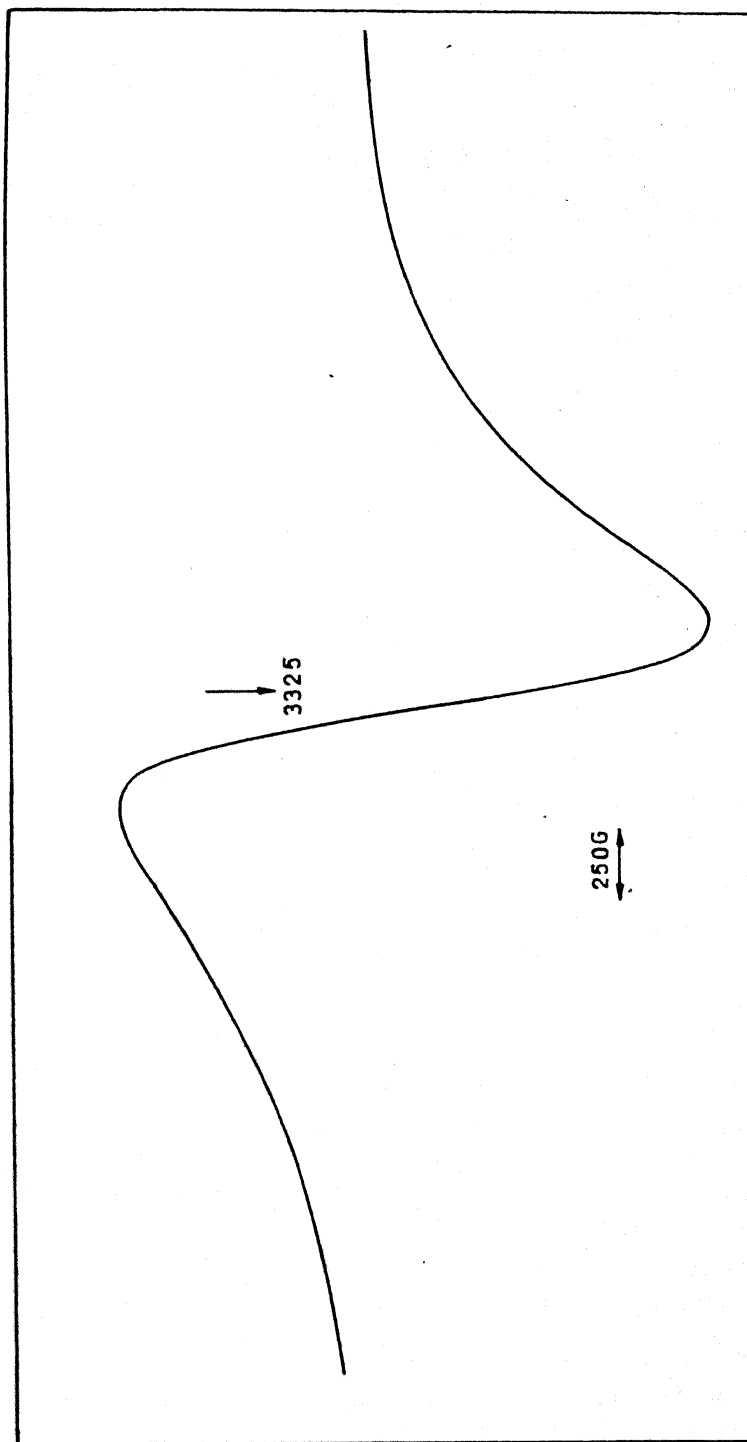
FIG. 4.4.2



Magnetic field (G)

EPR SPECTRUM OF POLYCRYSTALLINE $[(o\text{-phen})_2\text{MnS}_2\text{MoS}_2]$

FIG. 4.4.3



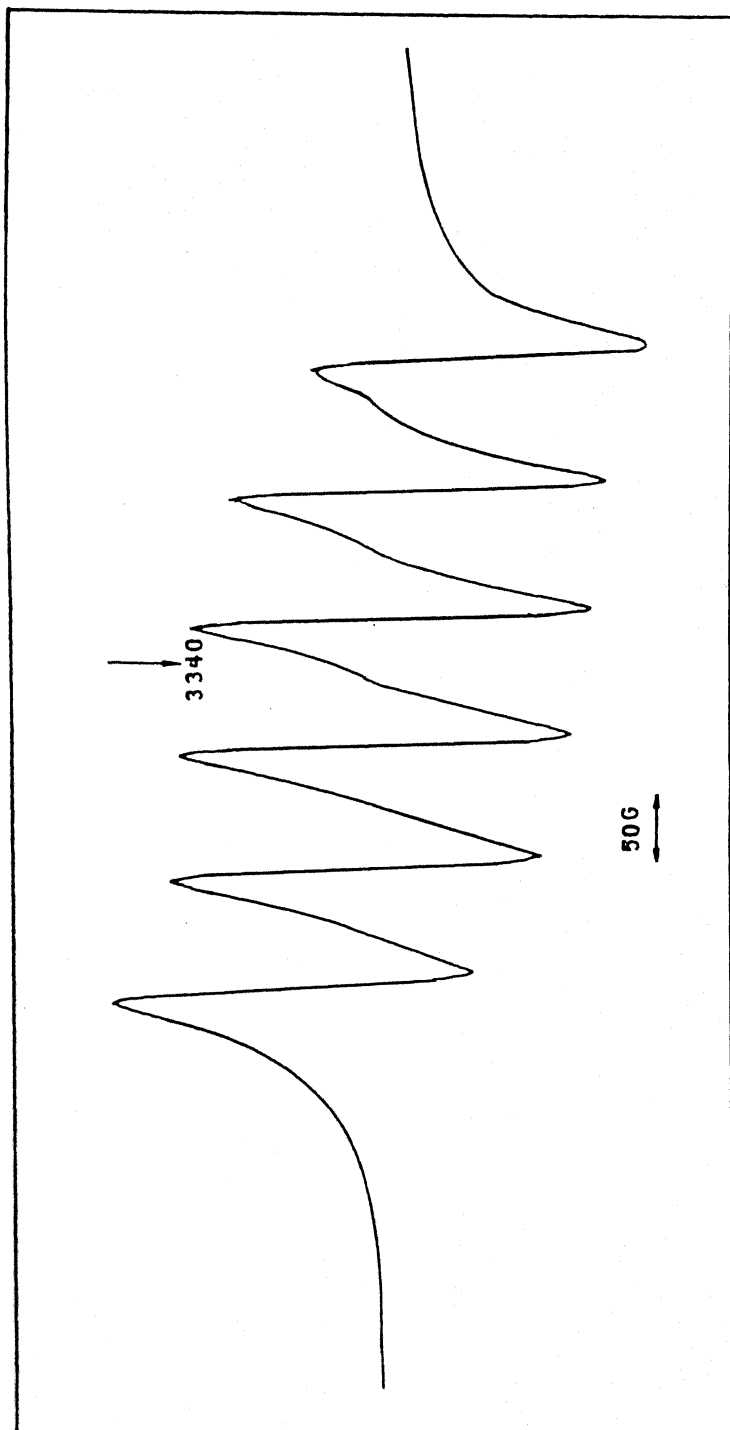
Magnetic field (G)

EPR SPECTRUM OF POLYCRYSTALLINE $[(bipy)_2MnS_2MoO_5]$

FIG. 4.4.4

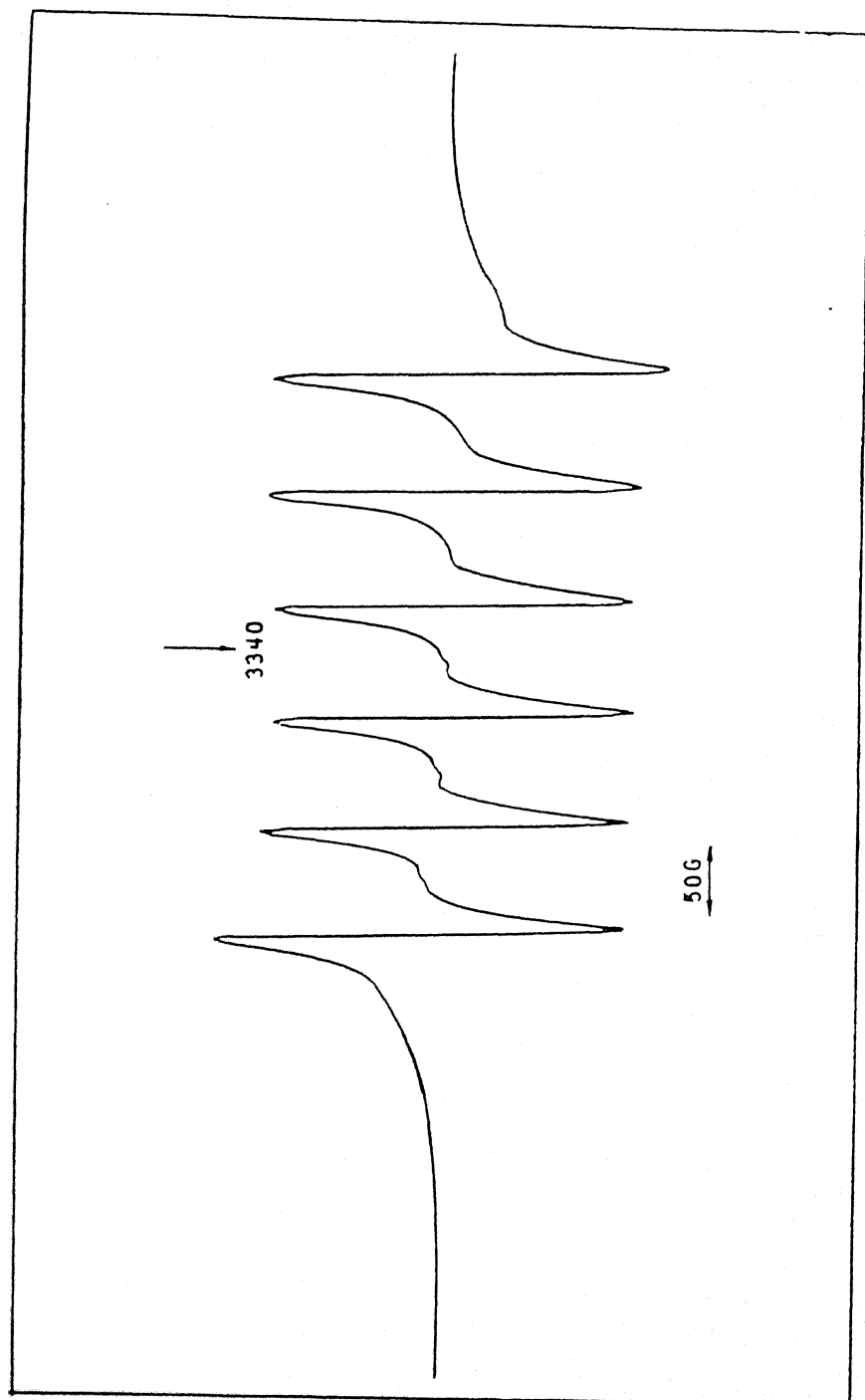
However, a very dilute solution of $[(bipy)_2MnWS_4]$ in DMF shows the characteristic six line hyperfine structure of the $+1/2 \longleftrightarrow -1/2$ transition with $g_{iso} = 2.001$ (Fig. 4.4.5). This is orientation independent as explained earlier. Here, the spin-spin exchange, dipolar interactions are removed by the physical separation of the complex molecules in the solvent. However, molecular tumbling persists. The magnetic dilution has also been achieved in solid state by doping Mn(II) in the analogous Co(II) complex, considering the fact at room temperature, Co(II) resonances are extremely broad. In this case (Fig. 4.4.6) between two hyperfine lines, we observe also the quadrupole induced forbidden transitions ($\Delta M_S \neq 1$). These lines are almost buried in noise and controlled dilution studies are required to resolve this feature. Due to the difficulty in obtaining single crystals of these complexes, we could not evaluate Zero field splitting parameters. Other observed EPR parameters (g and A values) are reported in the Table 4.6. One may conclude the following from these data:

- i) Mn(II) exists in an almost perfect octahedral environment (isotropic spectra, $g \approx g_e$).
- ii) There is a near constancy in the g and A values of all the complexes irrespective of the nature of the ligands. However, to understand the complete crystal field nature, single crystal work has to be done to evaluate the Zero field parameters D and E , as these are more sensitive to structural environment.



Magnetic field (G)
EPR SPECTRUM OF $[(\text{bipy})_2\text{MnS}_2\text{WS}_2]$ IN DMF

FIG. 4.4.5



Magnetic field (G)

EPR SPECTRUM OF POLYCRYSTALLINE $[(\text{bipy})_2\text{MnS}_2\text{WS}_2]$
DOPED IN $[(\text{bipy})_2\text{CoS}_2\text{WS}_2]$

FIG. 4.4.6

Table 4.6

EPR spectral data of Mn-thiometallate complexes

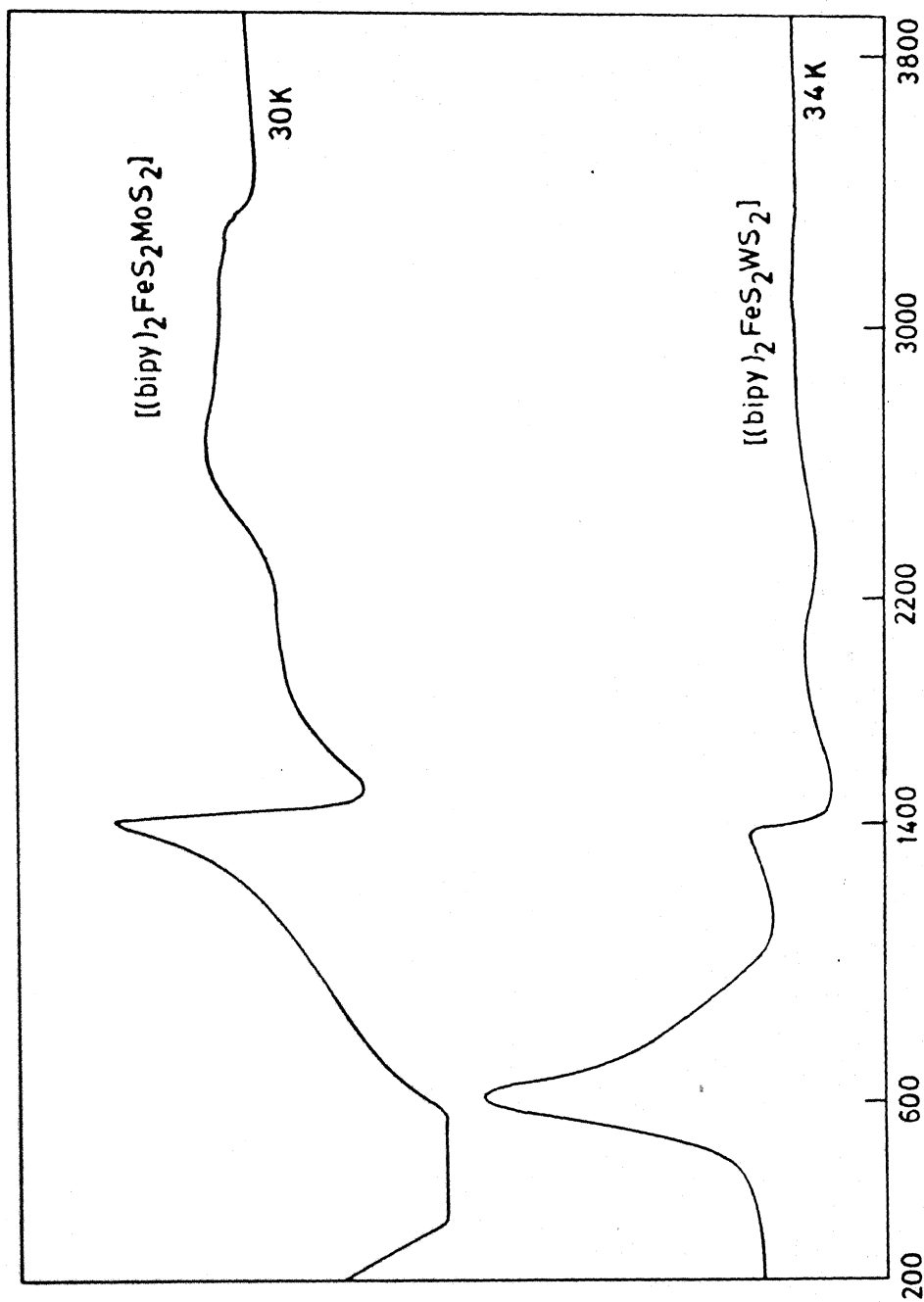
Complex	g_{av}	A_{av} (gauss)	Ref.
$[(bipy)_2MnS_2MoS_2]$	2.03	---	This work
$[(bipy)_2MnS_2WS_2]$	2.145	---	This work
$[(bipy)_2MnS_2MoOS]$	2.021	---	This work
$[(o-phen)_2MnS_2MoS_2]$	2.015	---	This work
$[(o-phen)_2MnS_2WS_2]$	2.012	---	This work
$[(o-phen)_2MnS_2MoOS]$	2.023	---	This work
$[(bipy)_2MnS_2WS_2]$ in DMF	2.001	92.6	This work
$[(bipy)_2MnS_2WS_2]$ doped in $[(bipy)_2CoS_2WS_2]$	2.002	84	This work
$[Mn(PMT)_6](ClO_4)_2$ doped in $[Fe(PMT)_6](ClO_4)_2$	2.001	84.4	178

PMT = pentamethylenetetrazole

4.4.3 EPR spectra of Fe-thiometallates

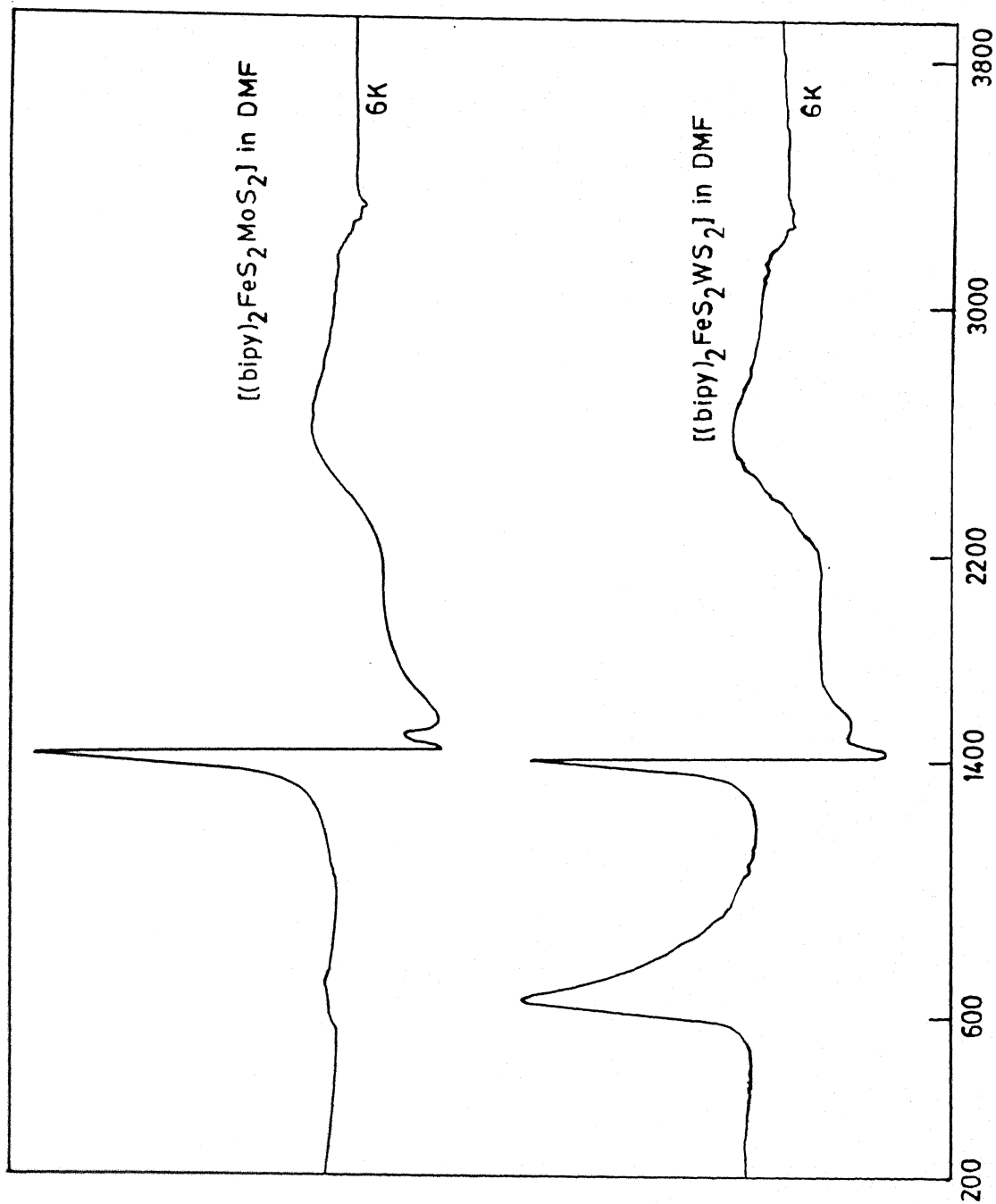
The low temperature EPR spectra of the complexes $[(bipy)_2FeS_2MS_2]$ ($M=Mo, W$) have been recorded both in the solid state and in frozen DMF solution (Fig. 4.4.7 and 4.4.8). The lines in the frozen DMF solution spectra are sharper than in the polycrystalline specimen spectrum and this can be attributed to dilution effect. The polycrystalline specimen spectra of both the complexes exhibit an EPR signal at $g=4.218$ and at high fields a very weak signal at $g\approx 2$. The EPR spectrum of the W complex is identical to that of its Mo analog but for a very strong resonance at low magnetic fields $g\approx 9.93$. This is weak to the extent of invisibility in the Mo complex. While it is very definite that all the above mentioned resonances occur in the Fe site, a definite assignment is not easy. An oxidation state of Fe(III) can be ruled out as this will require a Fe(III)-(V) ($M=Mo, W$) formulation for the metal centers in the complexes. If this were so, the EPR active M(V) signals should have been observed. Since, no signals have been observed in the room temperature spectra, the presence of Fe(III) is ruled out.

In iron-thiometallate chemistry, well resolved EPR spectra for only two linear [Fe-Mo-S] complexes have been reported to our knowledge [103,115]. The low temperature EPR spectrum of the trianionic complex $[Fe(MoS_4)_2]^{3-}$ in NMF exhibits resonances at $g\approx 4.38$, 3.42 and 2.06. The spectrum is very solvent dependent. In H_2O the same complex shows resonances at $g=5.15$, 2.52 and 1.71. This has been attributed to arising from a $S=3/2$ ground state and the complex has been formulated as a Fe(I) complex



LOW TEMPERATURE EPR SPECTRA

FIG. 4.4.7



LOW TEMPERATURE EPR SPECTRA
FIG. 4.4.8

bound to two Mo(VI) on either side. The trinuclear complex $[S_2MoS_2FeS_2Fe(SPh)_2]^{3-}$ also exhibits a narrow isotropic signal at $g=2.005$ consistent with a $S=1/2$ ground state in the low temperature EPR spectra.

In our case the presence of an Fe(I) center in the complex $[(bipy)_2FeS_2MoS_2]$ can be conveniently ruled out from analytical data. The only possibility for the presence of Fe(I) consistent with the analytical data is an Fe(I)-Mo(V) complex with a terminal disulfide ligand. The infrared spectral data rules out the presence of $[S_2]^{2-}$ and the room temperature EPR spectra rules out the presence of Mo(V). Hence, the resonances observed at low temperatures in the complexes $[(bipy)_2FeS_2MS_2]$ is due to the presence of an Fe(II) center. However, in the absence of Mössbauer data, the exact assignments of these transitions becomes very difficult, owing to the complicated highly anisotropic spectrum. It has been mentioned earlier that these complexes show interesting magnetic behavior. An important feature of the iron EPR is the anisotropy depicted in the spectrum varies quite a large extent even for small variations of the ligand field. The intense nature of the $g \approx 9.91$ resonance of the W complex may be attributed to this fact. A detailed description of the electronic properties of the $[(bipy)_2FeS_2MS_2]$ complexes remains to be developed.

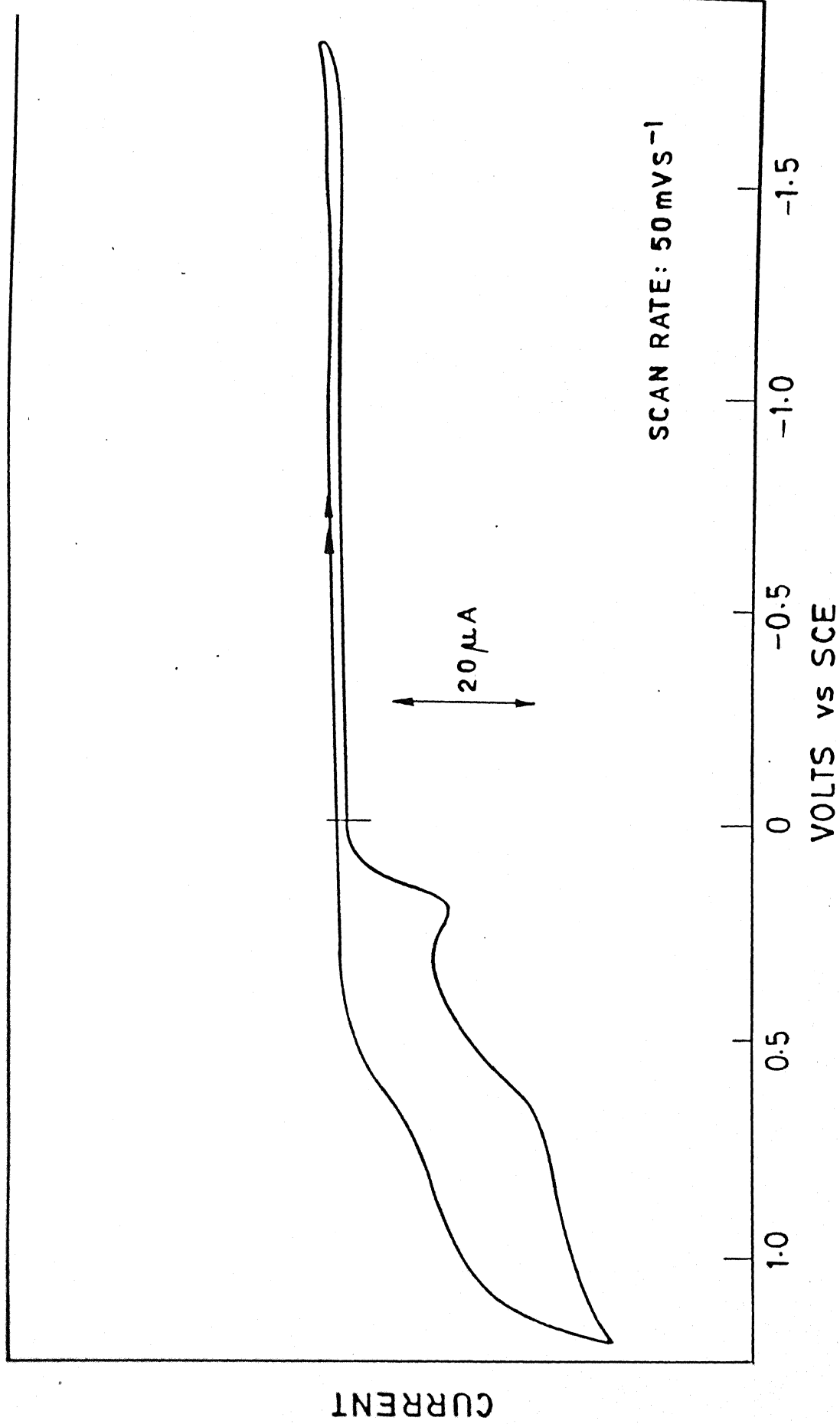
4.5 Cyclic voltammetry:

The cyclic voltammograms were recorded on a Bioanalytical Systems CV-27 voltammograph, in connection with a ClB-cell stand.

All the experiments were performed in a standard three electrode configuration using an auxiliary Pt electrode, a glassy carbon working electrode and a saturated calomel electrode under dinitrogen atmosphere at room temperature. Distilled DMF was used as the solvent and $[(C_4H_9)_4N]BF_4$ was used as the supporting electrolyte. The scans were recorded at a scan rate of 50 mV s^{-1} in the potential region +1.2 V to -2.00 V using a Omnigraphic 100 X-Y recorder.

The redox properties of the free and coordinated thiometallates have been studied by cyclic voltammetry. The cyclic voltammogram of Cs_2MoS_4 is presented in Fig. 4.5.1. The choice of the Cs salt is due to the fact that the redox events will be centered on the $[MoS_4]^{2-}$ moiety rather than Cs^+ , in the potential window scanned (+1.2 V to -2.00 V). In the negative scan, Cs_2MoS_4 does not undergo any redox event till -2 V. It has been reported recently that $[(C_2H_5)_4N]_2MoS_4$ undergoes irreversible reduction at a very high negative potential of -2.5 V in DMF [179]. However, the cyclic voltammogram of Cs_2MoS_4 exhibits two irreversible anodic waves at 223 mV and 691 mV in the positive scan. The first wave at 223 mV is due to the oxidation of the sulfide ligands as Mo is in its highest oxidation states. The corresponding oxotriithiomolybdate also exhibits an irreversible oxidation at around the same potential. The second anodic wave can be due to further oxidation.

In coordinated thiometallates a different trend is observed. The cyclic voltammogram of the complex $[(bipy)_2FeMoS_4]$ is presented in Fig. 4.5.2. This complex displays two



CYCLIC VOLTAMMOGRAM OF $[\text{Cs}_2\text{MoS}_4]$

FIG. 4.5.1

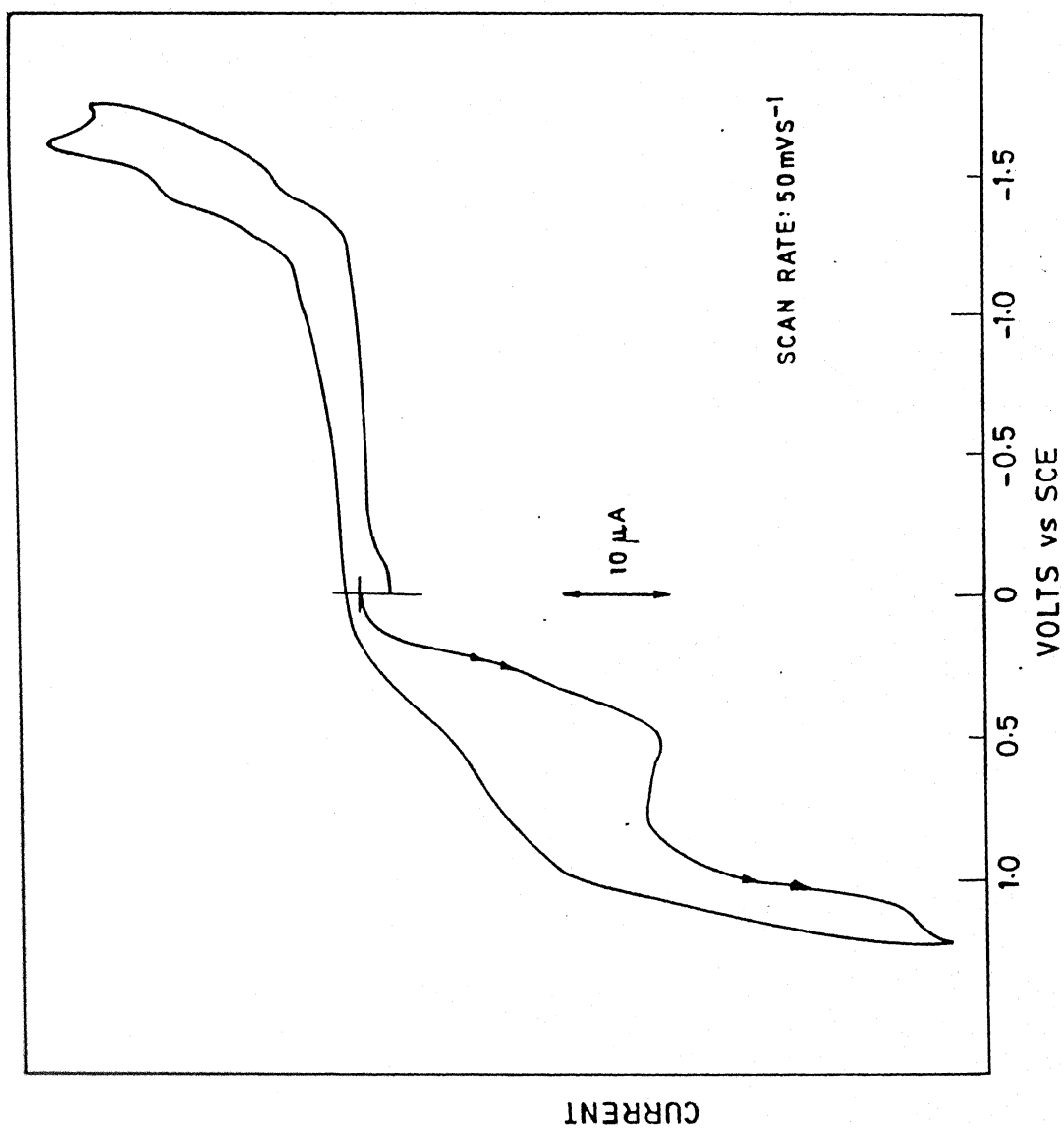
CYCLIC VOLTAMMOGRAM OF $[(\text{bipy})_2\text{FeS}_2\text{MoS}_2]$

FIG. 4.5.2

irreversible reductions in the negative scan. These can be attributed to the reduction of the organic amine. Similar irreversible anodic waves are also observed in the cyclic voltammograms of the corresponding Mn and Co complexes. These results are tabulated in Table 4.7. In all these complexes the reductions occur in the region -1.3 to -1.6 V. It has been reported that the complex $[(bipy)_2RuMoS_4]$ undergoes two quasi-reversible reductions at -1.5 V and -1.75 V respectively [130]. In the complexes $[(bipy)_2MnMS_4]$ (M=Mo, W) two irreversible anodic waves have been observed. These can be attributed to the oxidation processes $Mn(II) \rightarrow Mn(III)$ and $Mn(III) \rightarrow Mn(IV)$. It is interesting to note that for the complex $[(bipy)_2MnWS_4]$ the oxidations occur at a higher potential as compared to the corresponding Mo analog. The analogous Fe and Co complexes also exhibit two irreversible oxidations. In the case of the Fe and Co complexes the second oxidation occurs at a very high positive potential at around 1.1 V which is invariant. While the first oxidation can be termed as due to the oxidation process of the heterometal the second oxidation can be due to the oxidation of the terminal sulfides. This high positive potential may be an indication of the strong $M-S_{term}$ bond. This may probably be the reason, for the observation that a second metal cannot be ligated to the terminal sulfurs to form a trinuclear complex. In all the complexes the W analogs exhibit higher oxidation potentials as compared to their Mo counterparts, meaning by the W complexes are more stable. The electrochemical data are listed in Table 4.7.

Table 4.7

Electrochemical data of the synthesized complexes

Complex	$(E_P)_A$	$(E_P)_C$
Cs_2MoS_4	223,691	---
Cs_2MoOS_3	237,642	---
$[(bipy)_2MnMoS_4]$	127,455	-1320,-1465
$[(bipy)_2MnWS_4]$	400,673	-1292,-1474
$[(bipy)_2FeMoS_4]$	481,1110	-1351,-1536
$[(bipy)_2FeWS_4]$	619,1110	-1350,-1551
$[(bipy)_2FeMoOS_3]$	426,1082	-1351,-1517
$[(bipy)_2FeWOS_3]$	500,1073	-1360,-1564
$[(bipy)_2CoMoS_4]$	463,1020	-1277,-1480

 $(E_P)_A$ - Anodic peak potentials in mV vs SCE $(E_P)_C$ - Cathodic peak potentials in mV vs SCE

4.6 X-ray powder diffraction:

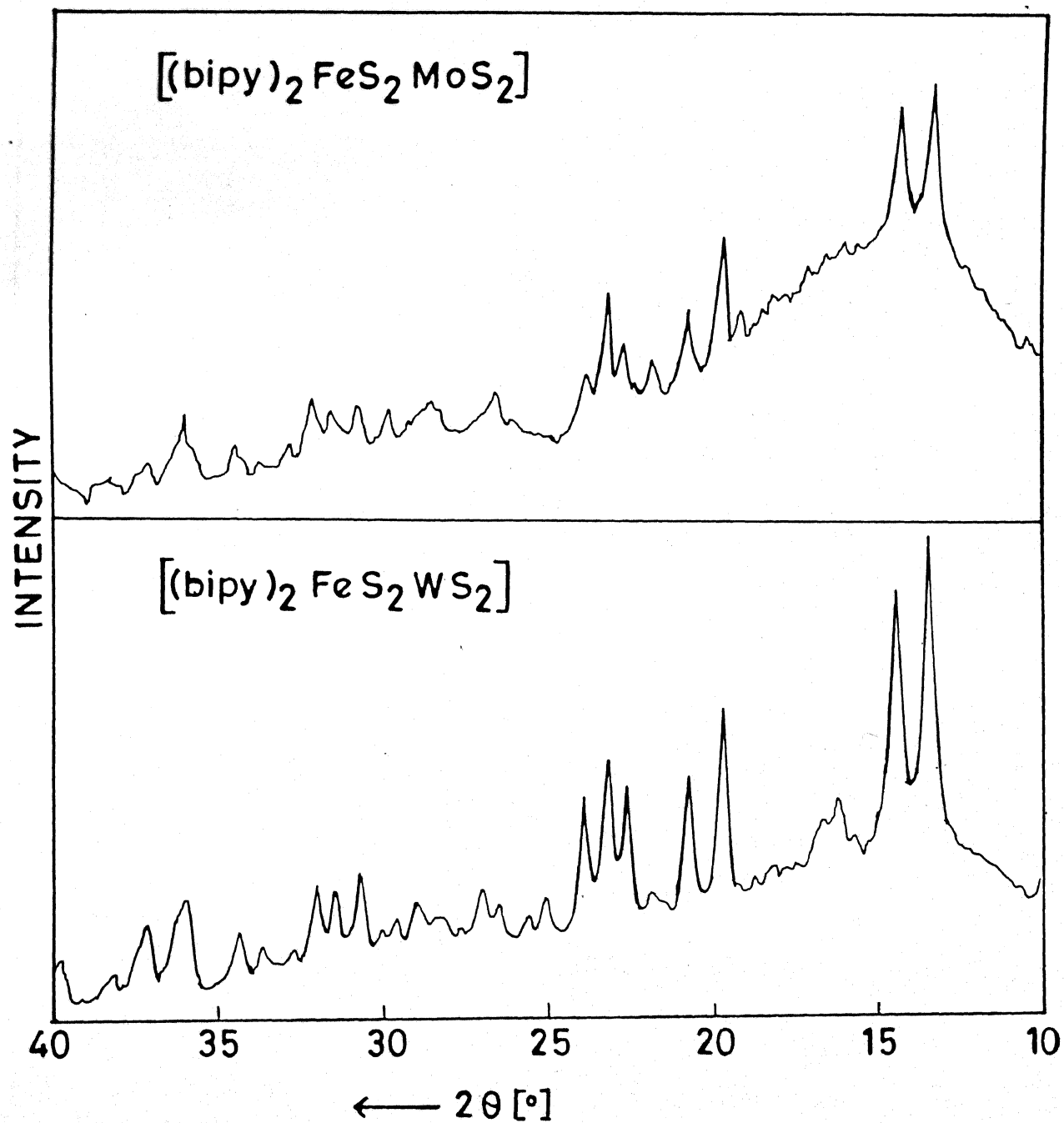
The X-ray powder patterns were recorded on a Siefert Isodebyeflex -2002 diffractometer using Cu-K α radiation with Ni filter. The powdered samples were packed on a perspex sample-holder.

The X-ray powder patterns of the complexes have been recorded to make a comparison between the structures of the tetrathiometallato and oxotrithiometallato complexes. The interplanar spacings for the most prominent peaks in the X-ray powder diffractograms are presented in Table 4.8. The X-ray powder patterns of some $[(bipy)_2M'MS_4]$ ($M'=Fe, Co, Ni$) complexes are presented in Figs. 4.6.1 to 4.6.5. Inspection of this data reveals that all the Fe, Co and Ni complexes show extremely similar patterns and hence they belong to the same structural class. The small differences in d spacings may be due to small differences in unit cell dimensions. The differences in intensities may be due to grinding and packing effects combined with the increase in metal scattering power in going from Mo to W. However, the $[(bipy)_2MnMS_4]$ complexes form a different structural class seen by the powder diffraction data. For example, the first reflection occurs around $\theta=5.9^\circ$ for the Mn complexes whereas in the corresponding Fe, Co and Ni complexes the first reflection is seen around $\theta=6.7^\circ$. However, it has been possible to dope the $[(bipy)_2MnWS_4]$ complex in the cobalt complex $[(bipy)_2CoWS_4]$ and the manganese doped cobalt complex exhibits a six line EPR spectrum characteristic of Mn(II) high spin system.

Table 4.8

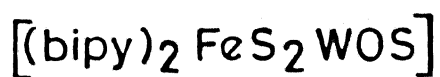
X-ray powder data

Complex	Interplanar (d) spacings of the most prominent peaks \AA
$[(\text{bipy})_2\text{FeS}_2\text{MoS}_2]$	6.60, 6.14, 4.50, 4.29, 3.91, 3.83, 2.91, 2.79, 2.50
$[(\text{bipy})_2\text{FeS}_2\text{WS}_2]$	6.60, 6.15, 4.53, 4.27, 3.92, 3.83, 3.72, 2.91, 2.84, 2.79, 2.50, 2.42
$[(\text{bipy})_2\text{FeS}_2\text{MoOS}]$	6.53, 6.08, 4.47, 3.87, 3.80, 2.88, 2.80, 2.76, 2.58, 2.03, 1.93, 1.72, 1.85
$[(\text{bipy})_2\text{FeS}_2\text{WOS}]$	6.55, 6.12, 4.48, 3.81, 3.69, 3.05, 2.89, 2.80, 2.77, 2.58, 2.39, 2.24, 2.18, 2.03, 1.94, 1.86, 1.72
$[(\text{bipy})_2\text{CoS}_2\text{MoS}_2]$	6.70, 6.19, 4.55, 4.33, 3.90, 3.75, 3.36, 2.83, 2.53
$[(\text{bipy})_2\text{CoS}_2\text{WS}_2]$	6.70, 6.17, 5.53, 4.55, 4.35, 3.97, 3.35, 3.10, 2.96, 2.84, 2.54
$[(\text{bipy})_2\text{NiMoS}_4]$	6.65, 6.19, 4.54, 4.33, 3.87, 3.39, 2.94, 2.82, 2.53, 2.06, 1.85, 1.75
$[(\text{bipy})_2\text{NiS}_2\text{WS}_2]$	6.73, 6.23, 4.55, 4.33, 3.93, 3.87, 3.75, 3.34, 2.94, 2.81, 2.53, 2.06, 1.85, 1.75
$[(\text{bipy})_2\text{NiS}_2\text{MoOS}]$	6.65, 6.10, 4.50, 4.30, 4.07, 3.83, 3.72, 3.32, 2.91, 2.77, 2.51, 2.13, 2.03, 1.94
$[(\text{bipy})_2\text{NiS}_2\text{WOS}]$	6.63, 6.10, 5.47, 4.48, 4.29, 3.90, 3.72, 2.80, 2.58, 2.40, 2.25, 2.03, 1.94, 1.86, 1.73
$[(\text{bipy})_2\text{MnMoS}_4]$	7.49, 6.15, 5.86, 4.97, 4.75, 4.62, 3.90, 3.80, 3.65, 2.82, 2.58, 2.43
$[(\text{bipy})_2\text{MnS}_2\text{WS}_2]$	7.49, 5.53, 4.98, 4.77, 4.48, 4.19, 3.91, 3.81, 3.66, 3.09, 2.84, 2.43



X-RAY POWDER DIFFRACTOGRAMS

FIG. 4.6.1

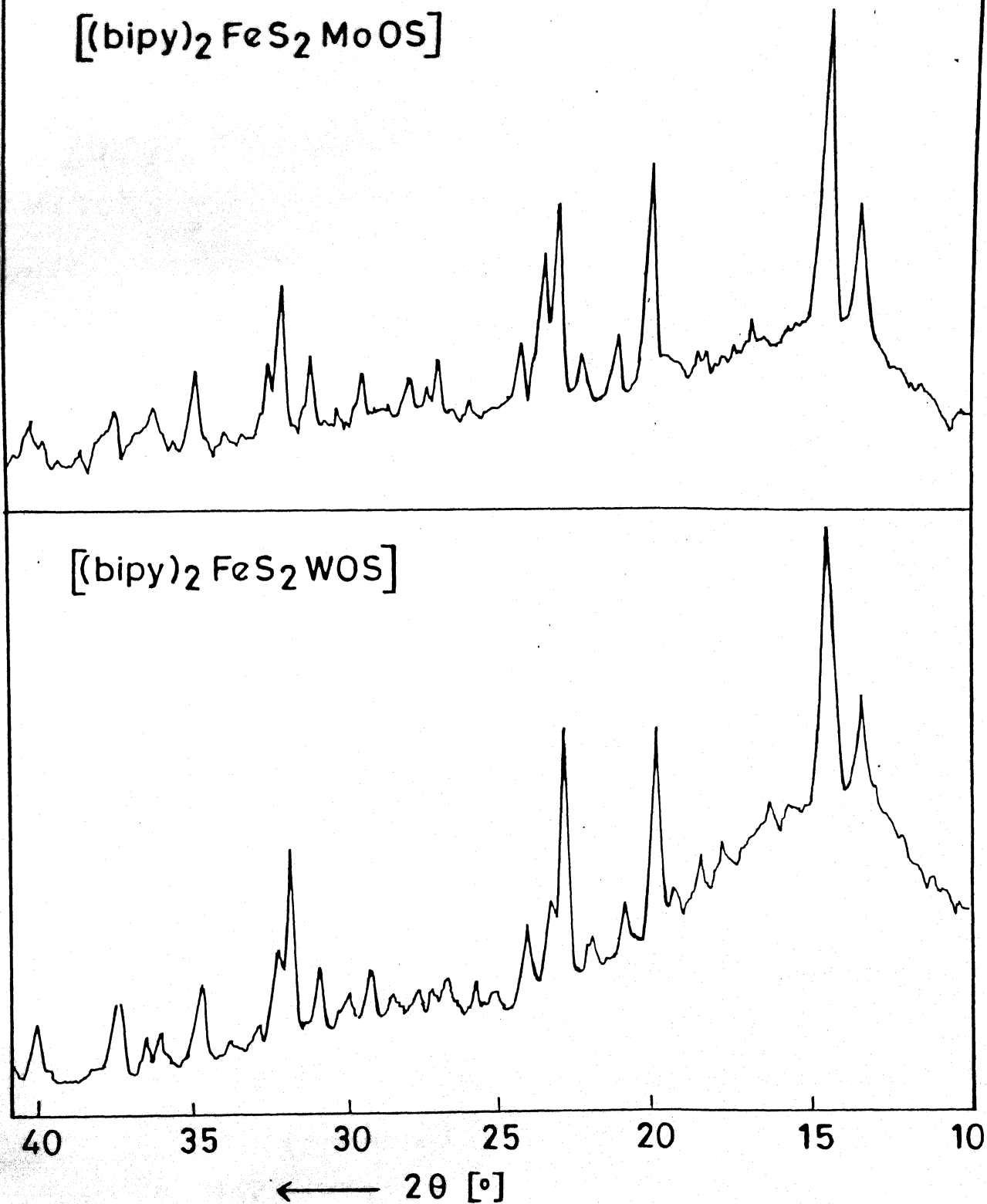


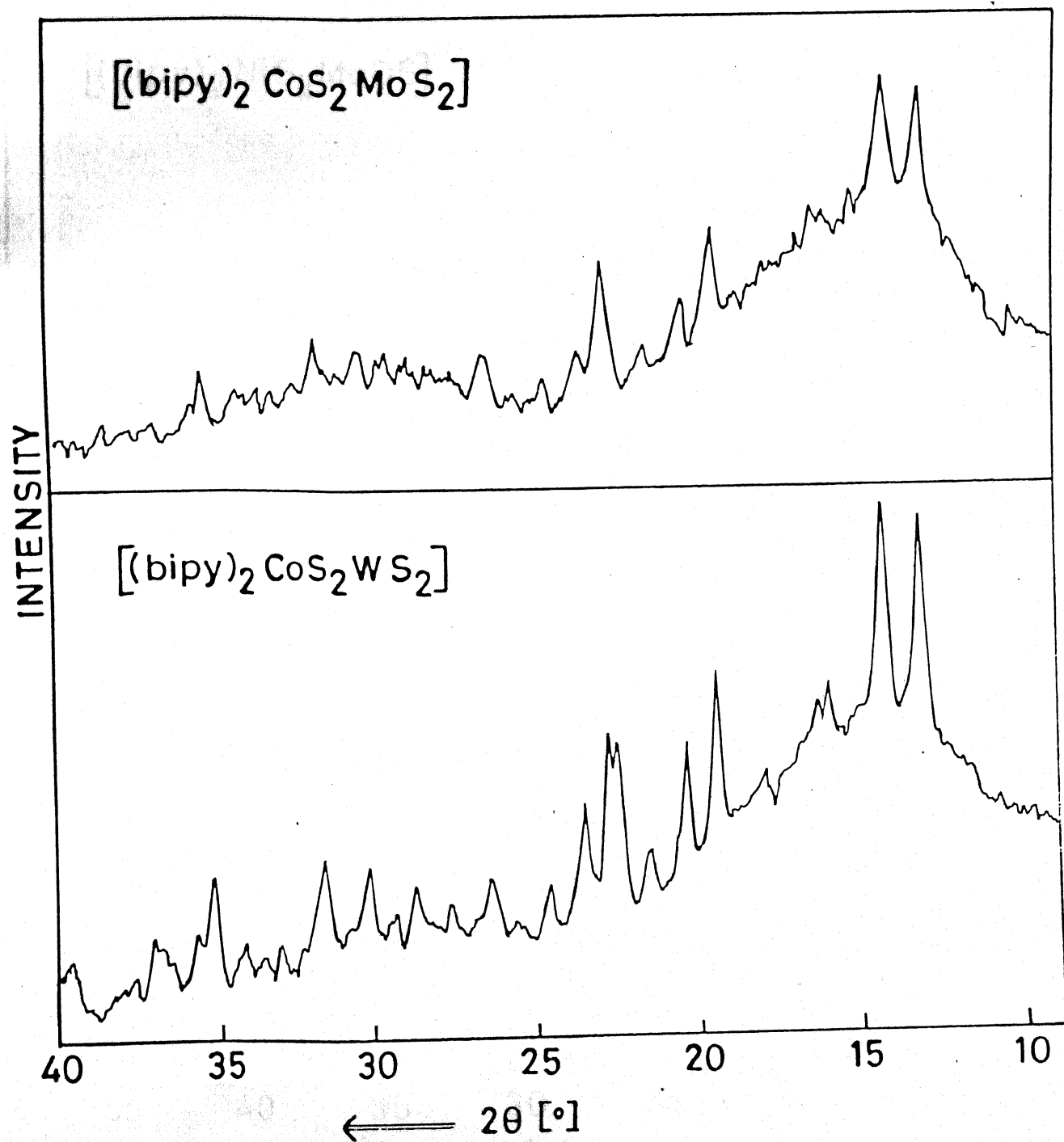
INTENSITY

40 35 30 25 20 15 10
← $2\theta [^\circ]$

X-RAY POWDER DIFFRACTOGRAMS

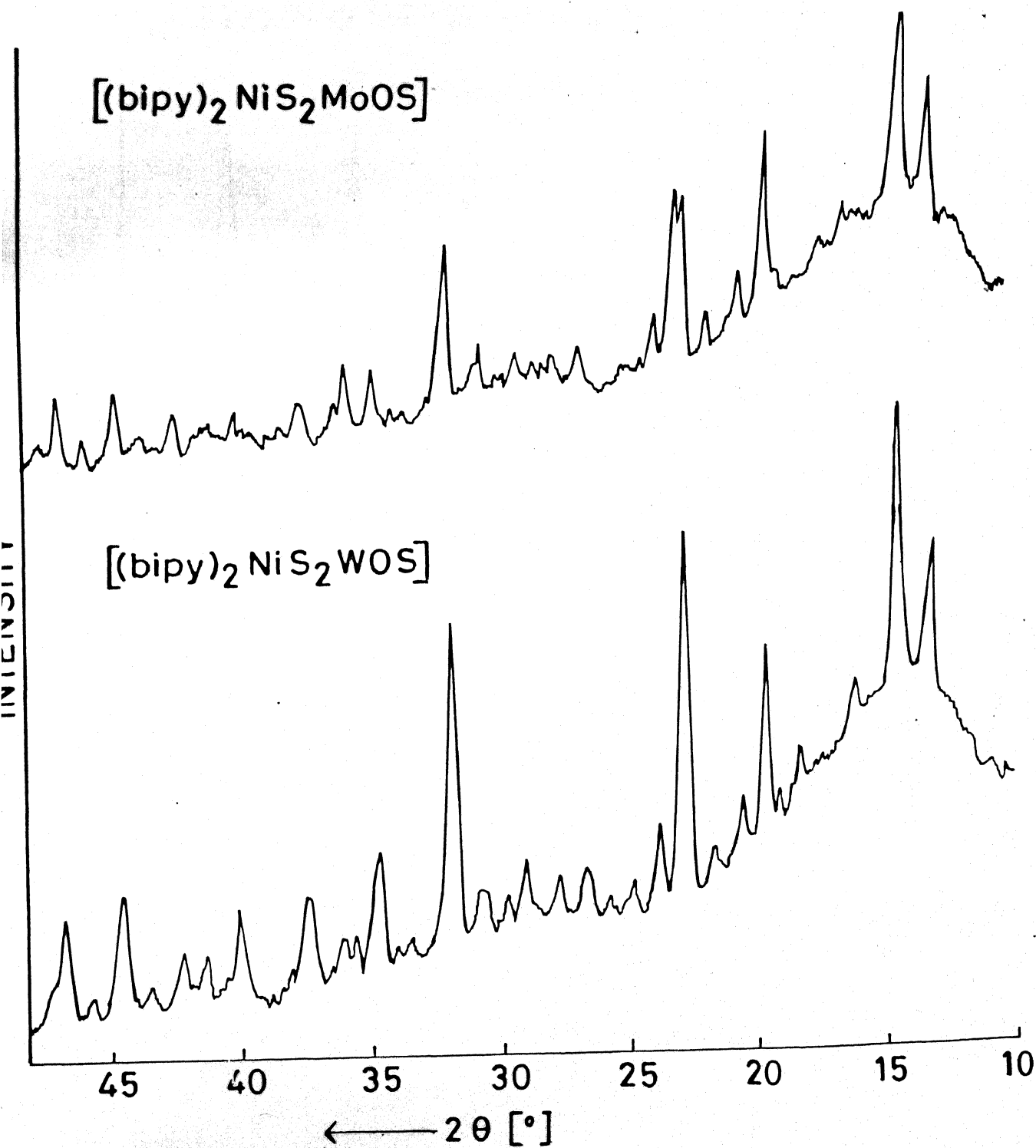
FIG. 4.6.2



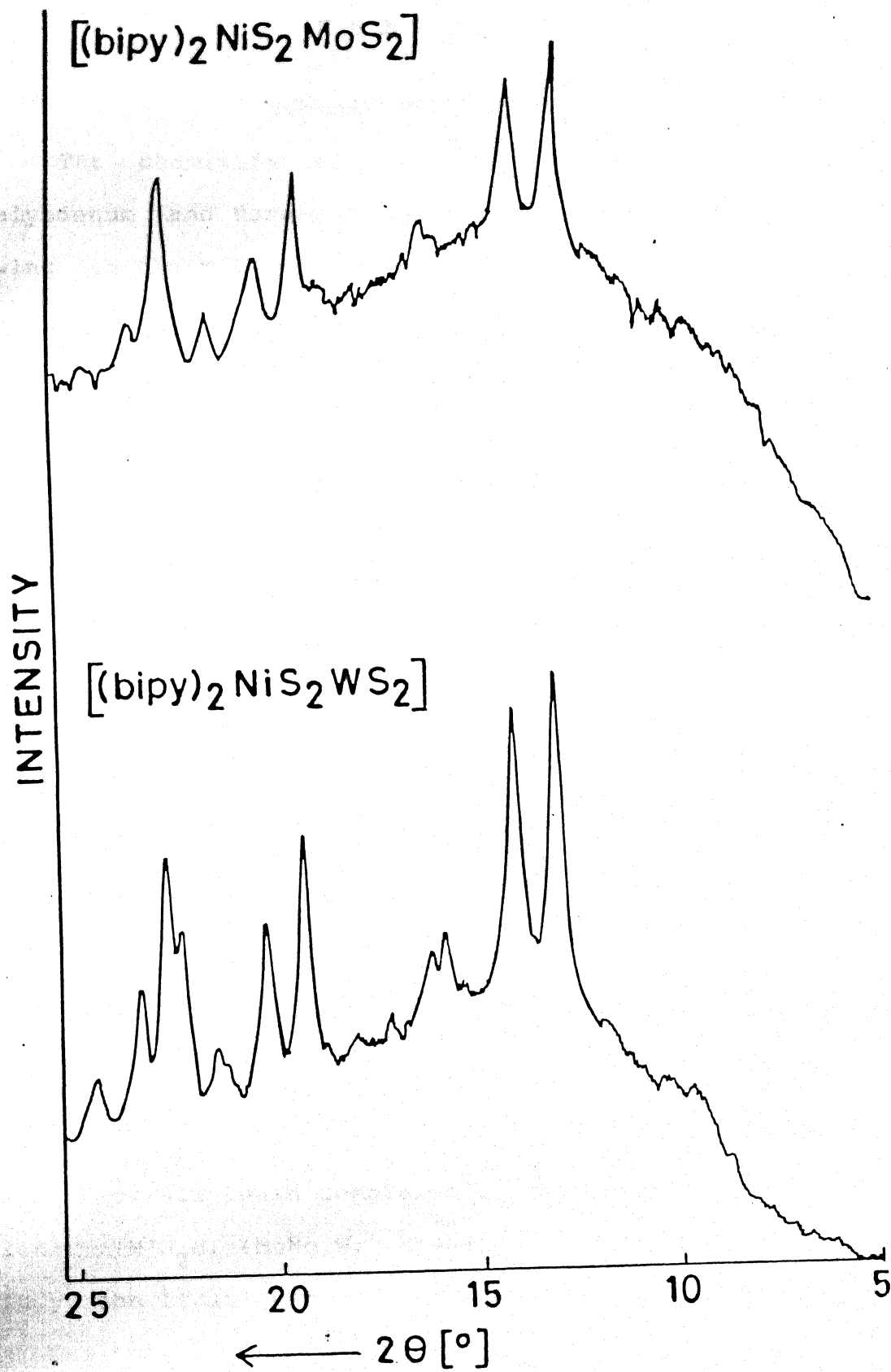


X-RAY POWDER DIFFRACTOGRAMS

FIG. 4.6.3



X-RAY POWDER DIFFRACTOGRAMS
FIG. 4.6.4



X-RAY POWDER DIFFRACTOGRAMS

FIG. 4.6.5

CHAPTER 5

SUMMARY AND CONCLUSIONS

The chemistry of the sulfur containing compounds of molybdenum and tungsten is becoming increasingly important owing to the relevance of these compounds in bioinorganic chemistry and catalysis. The thiomolybdates and thio-tungstates known since 1826 [8], have been the subject of study of many researchers in the last two decades and an extensive chemistry has been developed [11,12,74,75]. The thiomolybdates and thiotungstates referred to as thio-metallates in this thesis are prepared by exhaustive H_2S treatment of the corresponding oxometallates. The thio-metallates have been found to be very useful reagents in inorganic synthesis.

The reactions of the thiometallates leading to the formation of poly(thiometallates) and heterometal aggregates has been discussed in detail in the introductory chapter. An important aspect of the thiometallate chemistry is the formation of sulfur-bridged multimetallic complexes. A number of thiometallato complexes with various metal ions have been reported in the literature. The characteristic feature of all these complexes is the presence of the nearly planar $\{M'S_2M\}$ ($M=Mo,W$; M' =hetero metal) unit. In this study, the ligational behavior of the thiometallates has

synthesized and characterized. The complexes described in this work have the general formula $[L_2M'MS_4]$ (L=aromatic diimine; $M'=Mn, Fe, Co, Ni$; $M=Mo, W$). The corresponding oxo-trithiommetallate complexes have also been prepared for a comparative study. In the case of Ni(II), tetracoordinate complexes have also been prepared. The infrared spectra of the complexes are characteristic of the bidentate coordination of the thiommetallate ligands through two of the sulfur ends.

The iron-thiommetallate complexes described in this work exhibit interesting magnetic behavior. It is well known that the complex $[(bipy)_3Fe]^{2+}$ is diamagnetic. When one of the 2,2'-bipyridine ligands is replaced by the thiommetallate ligands, the resulting complexes have a very different magnetic behavior. The tetrathiommetallato complexes $[(bipy)_2FeS_2MS_2]$ have effective magnetic moments, less than the expected value for high spin Fe(II), whereas the oxo-trithiommetallato complexes are diamagnetic, which means that the oxotrichiommetallates are stronger ligands as compared to their tetrathio counterparts. The lowering of the magnetic moments is due to strong antiferromagnetic interactions in these complexes. The low magnetic moment (1.7 BM) values of the trinuclear complex $[S_2MoS_2FeS_2Fe(SPh)_2]^{3-}$ has been attributed to antiferromagnetic interactions [115].

However, the magnetic behavior of the complexes at different field strengths should be carried out in the low temperature region below the transition temperature (60 K) to understand the exact nature of these interactions.

The effective magnetic moment values of the cobalt, nickel and manganese complexes are also lower than the expected values for three, two and five unpaired electrons respectively. However, no temperature dependent magnetic studies have been performed on these complexes. It is very likely that the lowering of the magnetic moments may be due to antiferromagnetic interactions in these complexes also. A thorough study of the magnetic properties of all the complexes at different field strengths and various temperatures sounds a promising area of investigation for future work.

The reactions of substituted aromatic diimine complexes with thiometallates can be studied. Such studies will be useful in knowing the effect of substitution on the properties of the synthesized complexes.

The results of the present work can be summarized as follows :

- i) The reactions of aromatic diimine complexes of bivalent metal ions with thiometallates results in the formation of discrete 1:1 bimetallic complexes.

ii) In the neutral bimetallic iron-thiometallate complexes reported in this work Fe is hexacoordinate. The iron-thiometallate complexes exhibit interesting magnetic behavior.

iii) The cobalt and nickel complexes described in this work are the first examples of 1:1 complexes.

iv) It has been shown that the use of proper coligands can lead to the formation of Mn-thiometallate complexes. The manganese complexes reported in this work are the first examples of Mn-Mo/W complexes with sulfur bridges.

v) The tetracoordinate complexes $[L_2M'S_2MS_2]$ ($L=2,2'$ -bipyridine, $M'=Fe,Co,Ni$; $M=Mo,W$) are isostructural.

vi) The oxotrithiometallates are stronger ligands than tetrathiometallates.

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